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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on page 3 of the Journal cover. New tables will be announced from time to time as they become available.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1423

Part of Journal of Research of the National Bureau of Standards, Volume 27, October 1941

ISOLATION OF 1,2,3,4-TETRAMETHYLBENZENE, 5,6,7,8-TETRAHYDRONAPHTHALENE, 1-METHYL-5,6,7,8-TETRAHYDRONAPHTHALENE, AND 2-METHYL-5,6,7,8-TETRAHYDRONAPHTHALENE FROM PETROLEUM [1] [2]

By Beveridge J. Mair and Anton J. Streiff [3]

ABSTRACT

This paper reports the isolation of four additional aromatic hydrocarbons from the kerosene fraction of the petroleum being investigated by the American Petroleum Institute Research Project 6. Their separation was accomplished by a combination of the physical methods of fractionation of azeotropic distillation and crystallization. "Best" lots of each of these four hydrocarbons from petroleum were prepared, and synthetic lots of three of them were purified for purposes of identification and determination of properties. The amounts of impurity in these various lots of material were determined as follows, in mole fraction:

Hydrocarbon	From petroleum	From synthetic material
1,2,3,4-Tetramethylbenzene	0.0006 ±0.0001	
5,6,7,8-Tetrahydronaphthalene	.015 ± .002	0.0057 ±0.0008
1-Methyl-5,6,7,8-tetrahydronaphthalene	.0029 ± .0004	.0034 ± .0005
2-Methyl-5,6,7,8-tetrahydronaphthalene	.0046 ± .0007	.031 ± .004

Values of certain physical properties of these four hydrocarbons, all extrapolated to zero impurity, were determined as follows:

[1] Presented before the Division of Petroleum Chemistry at the meeting of the American Chemical Society at Atlantic City, N. J., September 8 to 12, 1941.

[2] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received.

[3] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

Property	1,2,3,4-Tetramethylbenzene		5,6,7,8-Tetrahydronaphthalene	
Boiling point at 760 mm, °C	205. 04	±0. 03	207. 57	±0. 10
Freezing point in air at 1 atm, °C	−6. 25	±0. 01	−35. 80	±0. 02
Density at 25° C, g/ml	0. 9015	±0. 0001	0. 9662	±0. 0002
Refractive index at 25° C:				
n_C	1. 51362	±0. 00007	1. 53466	±0. 0001
n_D	1. 51811	±0. 00007	1. 53919	±0. 0001
n_F	1. 52923	±0. 00007	1. 55065	±0. 0001
Specific dispersion at 25° C $(n_F-n_C)/d$	0. 01732	±0. 00005	0. 01655	±0. 0001

Property	1-Methyl-5,6,7,8-tetrahydronaphthalene		2-Methyl-5,6,7,8-tetrahydronaphthalene	
Boiling point at 760 mm, °C	234. 35	±0. 05	229. 03	±0. 05
Freezing point in air at 1 atm, °C	−22. 90	±0. 03	−39. 75	±0. 03
Density at 25° C, g/ml	0. 9682	±0. 0002	0. 9500	±0. 0002
Refractive index at 25° C:				
n_C	1. 53738	±0. 00010	1. 52920	±0. 0001
n_D	1. 54190	±0. 00010	1. 53365	±0. 0001
n_F	1. 55325	±0. 00010	1. 54498	±0. 0001
Specific dispersion at 25° C $(n_F-n_C)/d$	0. 01639	±0. 00005	0. 01662	±0. 0000

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I. INTRODUCTION

This paper constitutes the second report of the work on hydrocarbons in the kerosene fraction of petroleum begin carried on at this Bureau as part of the work of the American Petroleum Institute Research Project 6. There are described the isolation and identification of 1,2,3,4-tetramethylbenzene, 5,6,7,8-tetrahydronaphthalene, 1-methyl-5,6,7,8-tetrahydronaphthalene, and 2-methyl,5,6,7,8-tetrahydronaphthalene.

II. OUTLINE OF THE INVESTIGATION

The diagram in figure 1 shows schematically the last few steps in the work previously reported [1][4] and the steps in the work covered by this report. There has been given in detail in the first report [1] the method of obtaining the aromatic fractions shown in the block at the head of figure 1, by extraction and adsorption from a series of narrow-boiling kerosene fractions which distilled between 114° and 144° C at 56 mm Hg (approximately 200° to 230° C at 760 mm Hg), together with a description of the distillation at 56 mm of these aromatic fractions and the isolation of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene by crystallization. The work covered by the present report begins with a distillation at 56.8 mm Hg and the production of the second series of constant-boiling fractions shown in figure 1. Then by azeotropic distillation and fractional crystallization, 1,2,3,4-tetramethylbenzene and 5,6,7,8-tetrahydronaphthalene were isolated from the fractions which distilled between 118° and 120.5° C at 56.8 mm Hg; 2-methyl-5,6,7,8-tetrahydronaphthalene from the fractions which distilled between 137° and 140° C at 56.8 mm Hg; and 1-methyl-5,6,7,8-tetrahydronaphthalene from the fractions which distilled between 141° and 144° C at 56.8 mm Hg. As shown in figure 1, additional quantities of the 1- and 2-methylnaphthalenes were also isolated. The former was concentrated in a nearly pure condition by distillation alone in the fractions which distilled from 150° to 151° C at 56.8 mm Hg, while the latter was obtained by azeotropic distillation from the fractions distilling between 144° and 148° C at 56.8 mm Hg. The material distilling in the region from 148° to 150° C at 56.8 mm Hg consisted substantially of a mixture of 1- and 2-methylnaphthalenes.

[4] Figures in brackets indicate the literature references at the end of this paper.

FIGURE 1.—*Schematic outline of the investigation.*

III. SYSTEMATIC DISTILLATION AND SOME PROPERTIES OF THE DISTILLATION FRACTIONS

As stated in the preceding paragraph, the work covered by this report began with the systematic distillation at 56.8 mm Hg and the production of the second series of distillate fractions shown in figure 1. This distillation was performed in a column which had a rectifying section 2.5 by 280 cm and a separating efficiency corresponding to about 100 theoretical plates [2]. The reflux ratio was about 40 to 1, and the distillate was removed at a rate of about 9 ml per hour and collected in fractions of 50 ml.

Figure 2 gives the distribution by volume of the distillate with respect to the boiling point at 56.8 mm, and also shows the corresponding variation of the refractive indices of the distillate fractions. The large volume and high refractive indices in the region 118° to 120.5° C, from which 1,2,3,4-tetramethylbenzene (prehnitene) and 5,6,7,8-tetrahydronaphthalene (tetralin) were isolated, may be observed. Similarly, the large volumes and high refractive indices from 137° to 140° C, and from 141° to 144° C, correspond to the regions from which 2-methyl-5,6,7,8-tetrahydronaphthalene and 1-methyl-5,6,7,8-tetrahydronaphthalene, respectively, were isolated. The very high refractive indices of the fractions distilling above 145° C show the presence of considerable quantities of the 2- and 1-methylnaphthalenes.

IV. SEPARATION OF THE INDIVIDUAL HYDROCARBONS

The first step in the isolation of the individual hydrocarbons from the distillation fractions was the separation by azeotropic distillation (in one case by azeotropic distillation and fractional crystallization) of fractions which were very concentrated in the desired hydrocarbons. The pure hydrocarbons were then isolated from these concentrates by crystallization, as described in section V of this paper.

Since a detailed description of the procedures used in this laboratory for the separation of hydrocarbons by azeotropic distillation has recently been published [3], only a brief description will be given here. All the azeotropic distillations discussed here were performed at 217 mm Hg pressure with diethylene glycol monomethyl ether as the azeotrope-forming substance, in columns having a separating efficiency equivalent to about 100 theoretical plates. The reflux ratio was approximately 45 to 1 and the rate of removal of distillate about 15 ml per hour. Except in the case of 2-methylnaphthalene, sufficient azeotrope-forming substance was used so that all the hydrocarbon was obtained in the distillate. The oil was recovered from the azeotropic distillate fractions by washing with water. The boiling ranges of the azeotropic distillate fractions and their composition are given in table 1. The boiling point of diethylene glycol monomethyl ether at 217 mm Hg is 152.8° C.

TABLE 1.—*Boiling ranges and compositions of the azeotropic distillate*

	Aromatic fractions distilling at 56.8 mm over the ranges—			
	118° to 120.5° C	137° to 140° C	141° to 144° C	144° to 148° C
Boiling range of the azeotropic distillate at 217 mm, °C	141 to 147.5	144 to 151.7	145 to 151.7	147 to 152.8
Volume of oil in the azeotropic distillate, percent	55 to 50	30 to 20	25 to 15	18 to <1

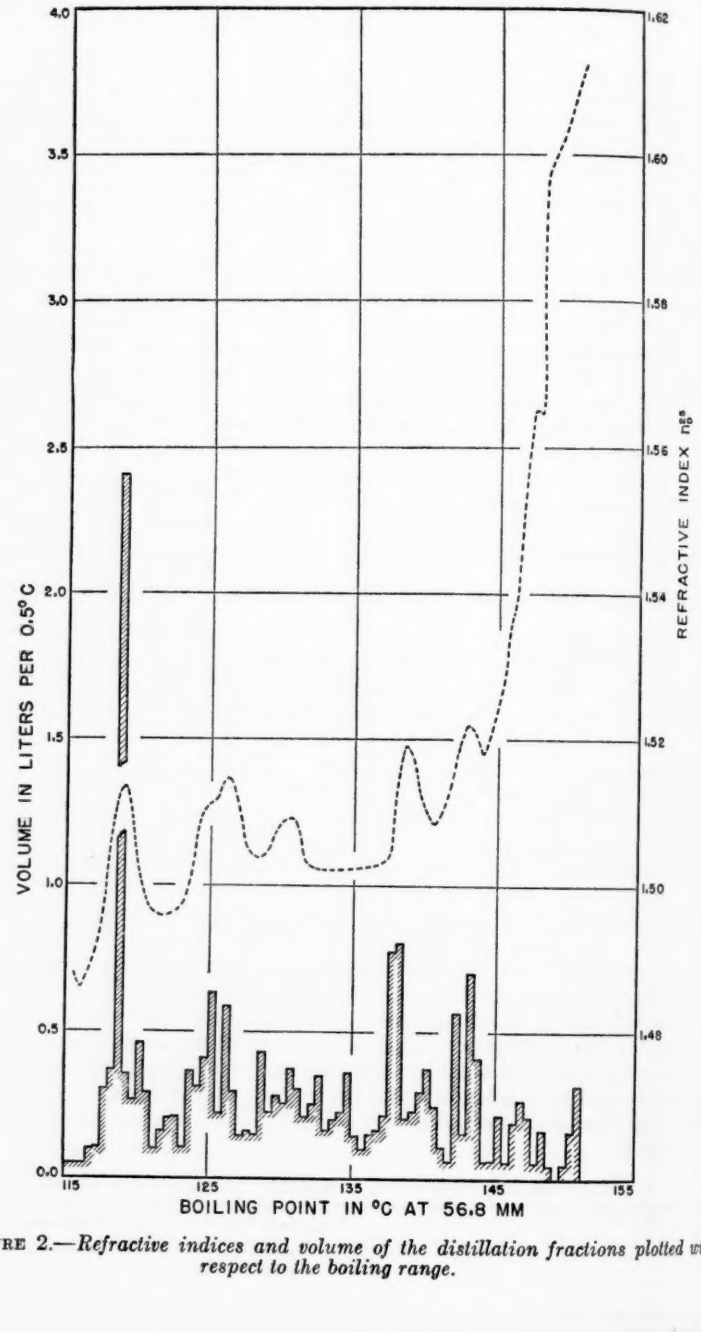

FIGURE 2.—*Refractive indices and volume of the distillation fractions plotted with respect to the boiling range.*

1. SEPARATION OF 1,2,3,4-TETRAMETHYLBENZENE AND 5,6,7,8-TETRAHYDRONAPHTHALENE

The separation resulting from the azeotropic distillation of a typical charge of material from the region 118° to 120.5° C at 56.8 mm Hg is shown in part 1 of figure 3, in which the refractive indices (n_D^{25}) of the oil fractions obtained from the azeotropic distillate are plotted with respect to the percentage of the hydrocarbon recovered from the distillate. The wide spread in the refractive indices of the fractions from this distillation is evident. The fractions with refractive indices between 1.51 and 1.52 crystallized readily (those with refractive indices around 1.518 as high as −22° C), and on fractionation by crystallization yielded 1,2,3,4-tetramethylbenzene. The fractions with indices of 1.534 or higher crystallized at about −40° C, and yielded 5,6,7,8-tetrahydronaphthalene on crystallization. Thus the charge was separated by azeotropic distillation into portions rich in 5,6,7,8-tetrahydronaphthalene and 1,2,3,4-tetramethylbenzene, respectively, and a portion rich in a mixture of the mono-, di-, or trialkylbenzenes. The separation of 1,2,3,4-tetramethylbenzene and 5,6,7,8-tetrahydronaphthalene from all the fractions distilling in the region from 118 ° to 120.5° C at 56.8 mm Hg was accomplished by azeotropic distillation, followed by the separation of 1,2,3,4-tetramethylbenzene from the fractions with indices between 1.51 and 1.52 by crystallization from dichlorodifluoromethane and centrifuging.[5] [6]

The fractions with refractive indices (n_{25}^{D}) above 1.534 were reserved as 5,6,7,8-tetrahydronaphthalene concentrates, and the fractions with indices below 1.50 were considered to be substantially free from 1,2,3,4-tetramethylbenzene and to consist principally of mono-, di-, or trialkylbenzenes. All the other fractions, and the mother liquors from the crystallization of 1,2,3,4-tetramethylbenzene, were blended according to their refractive indices, redistilled azeotropically, and their resolution, by alternate crystallization and azeotropic distillation, into 1,2,3,4-tetramethylbenzene, 5,6,7,8-tetrahydronaphthalene, and material of low refractive index was continued as far as was practical.

2. SEPARATION OF 2-METHYL-5,6,7,8-TETRAHYDRONAPHTHALENE

The separation resulting from the azeotropic distillation of a typical charge of material from the region 137° to 140° C at 56.8 mm Hg (see fig. 2) is shown in part 2 of figure 3. The close approach of the values for the refractive indices of the distillate fractions from the last third of the distillation to the value for the refractive index of 2-methyl-5,6,7,8-tetrahydronaphthalene is apparent. The fractions with refractive indices (n_D^{25}) above 1.529 crystallized at about −50° C and were segregated as 2-methyl-5,6,7,8-tetrahydronaphthalene concen-

[5] The centrifuge used in this work was constructed by the International Centrifuge Co. of Boston, Mass. It was similar to one of their standard centrifuges (catalog No. 418), except that the draining chamber was provided with a double jacket to contain the refrigerant and was insulated. The metal basket was 5 inches in diameter and the maximum speed of rotation was 3,600 rpm. The crystals were retained on a 200-mesh wire cloth which was fitted within the basket. This centrifuge gave crystals exceptionally free from mother liquors and was satisfactory for operations down to about −80 ° C. In this investigation all the crystallizations were performed with the aid of this centrifuge.

[6] In preliminary experiments it was found that some of the fractions from the peak in volume distilling between 118° and 119° C (particularly those distilling from 118.7° to 118.9° C) at 56.8 mm Hg yielded crystals on cooling to about −55 ° C. Some 1,2,3,4-tetramethylbenzene was separated from these fractions by fractional crystallization. An attempt to concentrate the 1,2,3,4-tetramethylbenzene in the mother liquor by distillation to a point where crystallization could again be effectively employed proved unsuccessful.

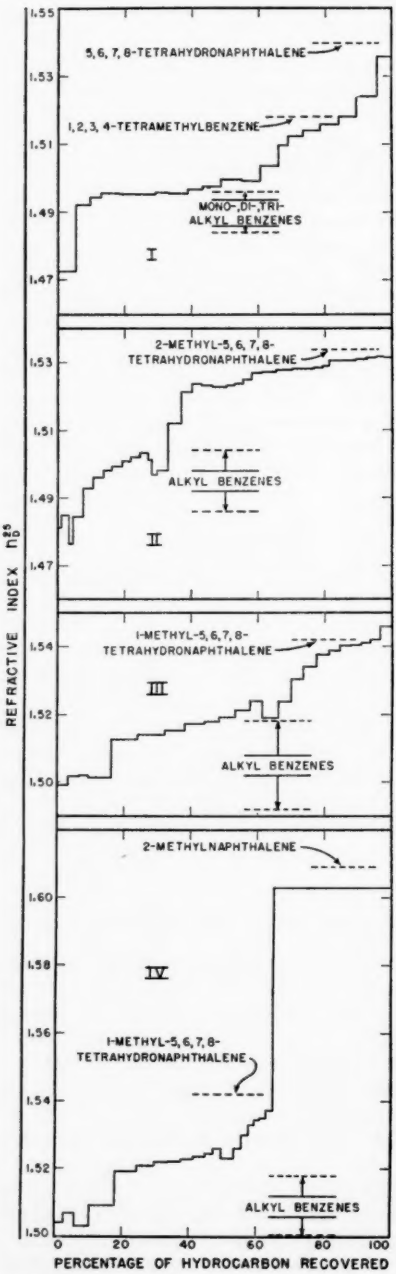

FIGURE 3.—*Diagrams illustrating the separation of various hydrocarbons by azeotropic distillation.*

trates, while the fractions with refractive indices below 1.505 were considered to consist substantially of alkylbenzenes. The intermediate fractions were blended on the basis of their refractive indices and were separated, as far as was practical, into the aforementioned portions by repeated azeotropic distillations.

3. SEPARATION OF 1-METHYL-5,6,7,8-TETRAHYDRONAPHTHALENE

The separation resulting from the azeotropic distillation of a typical charge of material from the region 141° to 144° C at 56.8 mm Hg (see fig. 2) is shown in part 3 of figure 3. It will be seen that the values for the refractive indices of the fractions which constituted the last 20 to 25 percent of the charge approach the value for the refractive index of 1-methyl-5,6,7,8-tetrahydronaphthalene. The fractions with indices from 1.534 to 1.542 froze readily at from −45 to −25° C and were segregated as 1-methyl-5, 6, 7, 8-tetrahydronaphthalene concentrates. The material of lower refractive index was redistilled azeotropically, and as much of the 1-methyl-5,6,7,8-tetrahydronaphthalene concentrates segregated as was practical.

4. SEPARATION OF 2-METHYLNAPHTHALENE

From the very high refractive indices of the material distilling in the region from 144° to 148° C at 56.8 mm Hg (see fig. 2), together with the fact that this was the region from which a substantial quantity of 2-methylnaphthalene had been separated in the previous investigation [1], it was obvious that these fractions still contained some 2-methylnaphthalene. As can be seen from part 4 of figure 3, an

excellent separation of this hydrocarbon is obtained by a single azeotropic distillation. In this distillation the percentage of oil in the distillate fractions decreases to less than 1 percent by volume as the hydrocarbon portion of the material remaining undistilled approaches 2-methylnaphthalene in composition. It is then unprofitable to continue the distillation further. The refractive indices shown in part 4 of figure 3 therefore refer to the oil obtained from the distillate fractions up to about 64 percent recovered, while the refractive index of the remainder refers to oil recovered from the residue. The oil from the residue which had a refractive index close to that of 2-methylnaphthalene, and which crystallized at 30° C (compare with 34.44° C for the freezing point of pure 2-methylnaphthalene), was segregated as 2-methylnaphthalene.

Besides the 2-methylnaphthalene actually separated by azeotropic distillation in the manner described, an additional quantity, which came from the comparatively small volume distilling in the region 148° to 150° C at 56.8 mm Hg (see fig. 2), was allocated to this compound. This material was substantially a mixture of 1- and 2-methylnaphthalenes and was allocated equally to these compounds (see section VI and table 6).

5. SEPARATION OF 1-METHYLNAPHTHALENE

The fractions distilling from 150° to 151° C (see fig. 2) had refractive indices (n_D^{25}) of 1.608 to 1.612. This material consisted substantially of 1-methylnaphthalene and was not separated further. In addition to this quantity, half the volume distilling from 148° to 150° C at 56.8 mm Hg was allocated to this compound (see section VI and table 6), as described in the preceding paragraph.

It may be pointed out that a mixture of 1- and 2-methylnaphthalenes may be obtained from crude petroleum in a very simple manner. It is necessary only to distill the kerosene fraction (or that portion containing the 1- and 2-methylnaphthalenes) in an efficient column, and then to select and distill azeotropically the narrow-boiling portion in which these two compounds are contained. In the azeotropic distillation, paraffins, naphthenes, alkylbenzenes, homologs of tetrahydronaphthalene, and a mixture of the 1- and 2-methylnaphthalenes will distill in the order mentioned. Thus the last fractions from the distillation, or the residue, will contain the 1- and 2-methylnaphthalenes, which can then be separated from one another as previously described [1].

V. PURIFICATION, IDENTITY, AND PHYSICAL PROPERTIES OF THE PURIFIED HYDROCARBONS

The purification of the individual hydrocarbons was accomplished by repeated fractional crystallization, using as starting material the concentrates whose separation has been described. 5,6,7,8-Tetrahydronaphthalene and its 1- and 2-methyl homologs were crystallized from solutions containing approximately 50 percent by volume of dichlorodifluoromethane. Owing to the relatively high freezing point (−6.25° C) of 1,2,3,4-tetramethylbenzene, dichlorodifluoromethane could not be used as a solvent in the final stages of purification of this compound. It was therefore crystallized from a solution containing

approximately 50 percent by volume of *n*-pentane. The purification processes were followed by measurements of the refractive index and occasionally by determinations of the freezing point.

Owing to the fragmentary and unreliable nature of the data on the physical properties of 5,6,7,8-tetrahydronaphthalene and its 1- and 2-methyl homologs (no data appear to have been published on 1-methyl-5,6,7,8-tetrahydronaphthalene), synthetic samples of these three hydrocarbons were obtained and purified.

Eastman's 5,6,7,8-tetrahydronaphthalene was used as the source for this substance. The "best" sample of this material was obtained after five crystallizations performed in the same manner as with the material from petroleum.

The synthetic samples of the 1- and 2-methyl-5,6,7,8-tetrahydronaphthalenes were obtained from N. L. Drake of the University of Maryland, who kindly prepared them by methods which left no doubt as to their identity. The 1-methyl-5,6,7,8-tetrahydronaphthalene, of which 131 ml was available, was distilled azeotropically with diethylene glycol monomethyl ether in the same manner as described for the material from petroleum.[7] Six fractions of hydrocarbon material, with a total volume of 83 ml and with refractive indices (n_D^{25}) between 1.5419 and 1.5423, taken from the middle of the distillate, were combined and crystallized once from dichlorodifluoromethane to obtain a "best" sample.

The 2-methyl-5,6,7,8-tetrahydronaphthalene, of which only 83 ml was available, was purified by azeotropic distillation and by a single crystallization of the best fractions from the distillate. Owing to the small amount of material, it was possible to obtain a "best" sample of only 32 ml. The purity of this sample was not high, but was sufficient for purposes of identification.

The "best" sample of each hydrocarbon, both the synthetic and that from petroleum, was distilled at a low pressure so that it was not heated above 60° to 70° C, and a small residue was discarded. The distillate was used for the determination of the physical properties.

The amounts of impurity in the best samples, as well as values of the freezing points for material with zero impurity, were estimated from time-temperature freezing and melting curves according to the procedure described previously [4]. In the case of 1,2,3,4-tetramethylbenzene and 5,6,7,8-tetrahydronaphthalene it was possible to estimate the amount of impurity from the freezing curve. However, in the case of 1-methyl-5,6,7,8-tetrahydronaphthalene and 2-methyl-5,6,7,8-tetrahydronathphalene the recovery from undercooling is extremely slow, and the freezing curves can not be used to determine the freezing point and estimate the amount of impurity. Instead, the freezing point and amount of impurity were determined from melting curves. The curves given in figure 4 illustrate this behavior for 2-methyl-5,6,7,8-tetrahydronaphthalene. In this figure the dashed lines represent the extrapolation necessary to determine the freezing point. The nearly vertical dashed line is an extrapolation of the liquid warming curve from a point above which it was certain that all the sample was in the liquid phase. There is also indicated by the value 0.083° C the difference in temperature of thermodynamic

[7] The distillation of such a small quantity of material in a large column was feasible only by the use of an azeotrope-forming substance which greatly increased the volume of distillate. (See reference [3]).

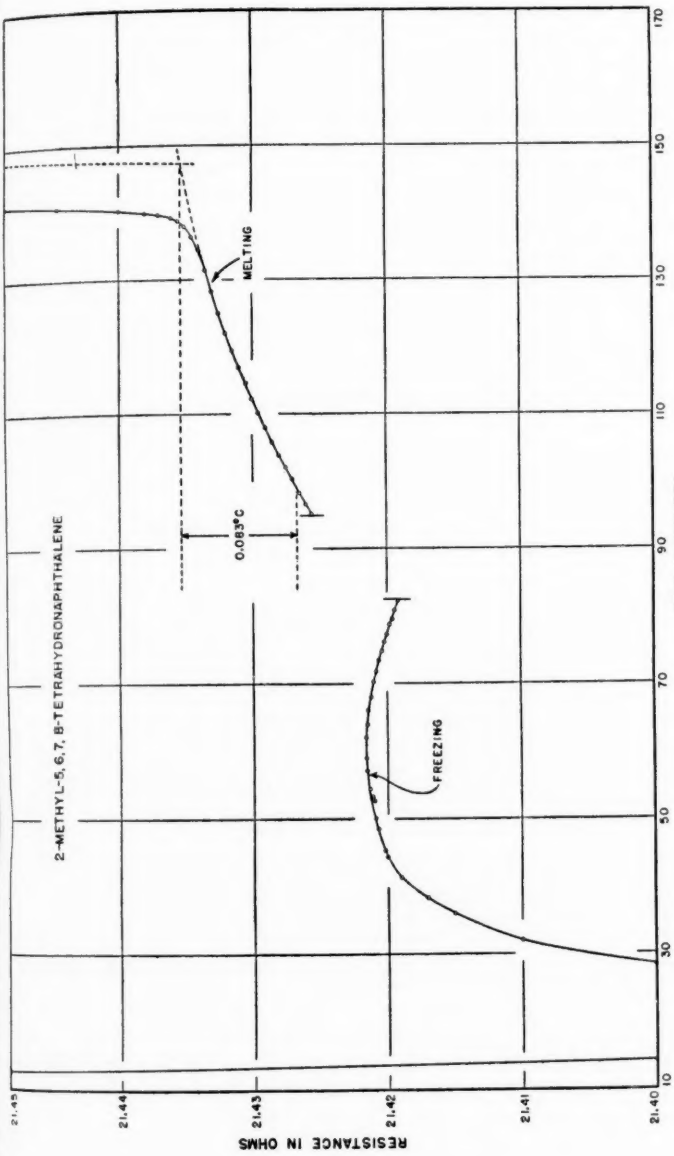

FIGURE 4.—*Portions of time-temperature freezing and melting curves for 2-methyl-5,6,7,8-tetrahydronaphthalene.*

equilibrium between the states having one-third and zero fraction of the substance in the crystalline phase.[8]

The properties of the best samples, both the synthetic ones and those from petroleum, together with values from previous investigations, are given in tables 2 to 5. The values of boiling point, refractive index, and density given for material of zero impurity are made the same as those for the "best" lot, but with an added uncertainty, because the processes of fractionation and purification tend to make the impurities, which are unknown, have very similar values of boiling point, refractive index, and density. The identity of the hydrocarbons from petroleum is established by the close agreement of their physical properties with the physical properties of the synthetic samples.

TABLE 2.—*Properties of 1,2,3,4-tetramethylbenzene*

Properties	Values from this investigation (material from petroleum)				Values from previous investigations		
	Actual "best" lot		Extrapolated to zero impurity		Auwers [5]	Smith and MacDougall [6] or MacDougall and Smith [7]	Jacobsen [8]
Amount of impurity, mole fraction	0.00058	±0.00006	0				
Boiling point [a] at:							
760 mm °C	205.04	±0.03	205.04	±0.03	203 to 204	204.4	20
217.2 mm °C	158.46	±0.03	158.46	±0.03		158.1	
57.3 mm °C	119.40	±0.05	119.40	±0.05		119.8	
Freezing point in air at 1 atm °C	−6.28	±0.01	−6.25	±0.01		−6.4	−4
Density [b] at:							
20° C g/ml	0.9053	±0.0001	0.9053	±0.0001	[d] 0.9014		
25° C g/ml	.9015	±0.0001	.9015	±0.0001			
Refractive index [c] at:							
20° C n_C	1.51563	±0.00005	1.51563	±0.00007	[e] 1.51458		
20° C n_D	1.52013	±0.00005	1.52013	±0.00007	[e] 1.51868		
20° C n_F	1.53133	±0.00005	1.53133	±0.00007	[e] 1.53029		
25° C n_C	1.51362	±0.00005	1.51362	±0.00007			
25° C n_D	1.51811	±0.00005	1.51811	±0.00007			
25° C n_F	1.52923	±0.00005	1.52923	±0.00007			
Refractive dispersion at:							
20° C (n_F-n_C)	0.01570	±0.00005	0.01570	±0.00005	0.01571		
25° C (n_F-n_C)	.01561	±0.00005	.01561	±0.00005			
Specific dispersion at:							
20° C $(n_F-n_C)/d$	.01734	±0.00005	.01734	±0.00005	.01736		
25° C $(n_F-n_C)/d$	.01732	±0.00005	.01732	±0.00005			

[a] Determined by B. J. Mair with the apparatus of C. B. Willingham and F. D. Rossini.
[b] Determined by the Capacity and Density Section of this Bureau.
[c] Determined by L. W. Tilton, of the Optical Instrument Section of this Bureau.
[d] Obtained by subtracting 0.0030 from the values reported at 16° C.
[e] Obtained by subtracting 0.00163 from the values reported at 16° C.

[8] The time at which a given fraction of the sample was in the crystalline phase was computed by means of eq 28 given in reference [4]. See also the discussion there.

TABLE 3.—*Properties of 5,6,7,8-tetrahydronaphthalene*

Properties	Values from this investigation				Values from previous investigations [a]		
	Material from petroleum		Purified synthetic material				
	Actual "best" lot	Extrapolated to zero impurity	Actual "best" lot	Extrapolated to zero impurity	Herz and Schuftan [9]	Auwers [10]	Adkins and Reid [11]
Amount of impurity, mole fraction	0.015 ±0.002	0	0.0057 ±0.0008	0			
Boiling point [a] at:							
760 mm °C	207.66 ±0.10		207.57 ±0.10	207.57 ±0.10	207.3		
217.2 mm °C			159.97 ±0.10	159.97 ±0.10	159.3		
57.3 mm °C			120.21 ±0.10	120.21 ±0.10	119.2		
Freezing point in air at 1 atm °C	−36.22 ±0.01	−35.79 ±0.03	−35.97 ±0.01	−35.80 ±0.02	−35.0		
Density [b] at:							
20° C g/ml	0.9705 ±0.0001		0.9702 ±0.0001	0.9702 ±0.0002	0.9693	0.971	
25° C g/ml	.9665 ±0.0001		.9662 ±0.0001	.9662 ±0.0002	.9655		
Refractive index [c] at:							
20° C n_C	1.53703 ±0.00005		1.53676 ±0.00005	1.53676 ±0.00015		[d] 1.53826	
20° C n_D	1.54161 ±0.00005		1.54135 ±0.00005	1.54135 ±0.00015		[d] 1.54283	
20° C n_F	1.55326 ±0.00005		1.55291 ±0.00005	1.55291 ±0.00015		[d] 1.55466	
25° C n_C	1.53496 ±0.00005		1.53466 ±0.00005	1.53466 ±0.00015			
25° C n_D	1.53952 ±0.00005		1.53919 ±0.00005	1.53919 ±0.00015			1.5395
25° C n_F	1.55097 ±0.00005		1.55065 ±0.00005	1.55065 ±0.00015			
Refractive dispersion at:							
20° C (n_F-n_C)	.01623 ±0.00005		.01615 ±0.00005	.01615 ±0.00010		0.01640	
25° C (n_F-n_C)	.01601 ±0.00005		.01599 ±0.00005	.01599 ±0.00010			
Specific dispersion at:							
20° C $(n_F-n_C)/d$	.01672 ±0.00005		.01665 ±0.00005	.01665 ±0.00010		0.01689	
25° C $(n_F-n_C)/d$	.01656 ±0.00005		.01655 ±0.00005	.01655 ±0.00010			

[a] Determined by B. J. Mair with the apparatus of C. B. Willingham and F. D. Rossini.
[b] Determined by the Capacity and Density Section of this Bureau.
[c] Determined by L. W. Tilton, of the Optical Instruments Section of this Bureau.
[d] Auwers [10] gives sets of values on three samples which differ substantially among themselves. These values were obtained by subtracting 0.00061 from the lowest set of values reported by Auwers at 21.4° C.
[e] See also references [14], [15], [16], and [17].

TABLE 4.—*Properties of 2-methyl-5, 6, 7, 8-tetrahydronaphthalene*

Properties	Values from this investigation				Values from previous investigations
	Material from petroleum		Purified synthetic material		
	Actual "best" lot	Extrapolated to zero impurity	Actual "best" lot		Krollpfeiffer and Schäfer [12]
Amount of impurity, mole fraction	0.0046 ±0.0007	0	0.031 ±0.004		
Boiling point [a] at:					
760 mm °C	229.03 ±0.05	229.03 ±0.05	229.06 ±0.05		224 to 22
217.2 mm °C	179.91 ±0.05	179.91 ±0.05			
57.3 mm °C	138.75 ±0.07	138.75 ±0.07			
Freezing point in air at 1 atm °C	−39.92 ±0.01	−39.75 ±0.03	−40.84 ±0.03		
Density [a] at:					
20° C g/ml	0.9537 ±0.0001	0.9537 ±0.0002	0.9543 ±0.0001		d 0.950
25° C g/ml	.9500 ±0.0001	.9500 ±0.0002	.9505 ±0.0001		
Refractive index [a] at:					
20° C n_C	1.53115 ±0.00005	1.53115 ±0.00010	1.53107 ±0.00005		[e] 1.5310
20° C n_D	1.53572 ±0.00005	1.53572 ±0.00010	1.53571 ±0.00005		[e] 1.5356
20° C n_F	1.54706 ±0.00005	1.54706 ±0.00010	1.54697 ±0.00005		[e] 1.5470
25° C n_C	1.52920 ±0.00005	1.52920 ±0.00010	1.52914 ±0.00005		
25° C n_D	1.53365 ±0.00005	1.53365 ±0.00010	1.53361 ±0.00005		
25° C n_F	1.54498 ±0.00005	1.54498 ±0.00010	1.54499 ±0.00005		
Refractive dispersion at:					
20° C (n_F-n_C)	0.01591 ±0.00005	0.01591 ±0.00005	0.01590 ±0.00005		0.0159
25° C (n_F-n_C)	.01578 ±0.00005	.01579 ±0.00005	.01585 ±0.00005		
Specific dispersion at:					
20° C $(n_F-n_C)/d$	.01668 ±0.00005	.01668 ±0.00005	.01666 ±0.00005		.0167
25° C $(n_F-n_C)/d$	.01661 ±0.00005	.01662 ±0.00005	.01668 ±0.00005		

[a] Determined by B. J. Mair with the apparatus of C. B. Willingham and F. D. Rossini.
[b] Determined by the Capacity and Density Section of this Bureau.
[c] Determined by L. W. Tilton, of the Optical Instruments Section of this Bureau.
[d] Obtained by subtracting 0.0037 from the value reported at 15.1° C.
[e] Obtained by subtracting 0.00198 from the values reported at 15.1° C.

TABLE 5.—*Properties of 1-methyl-5, 6, 7, 8-tetrahydronaphthalene*

Properties	Values from this investigation			
	Material from petroleum		Purified synthetic material	
	Actual "best" lot	Extrapolated to zero impurity	Actual "best" lot	Extrapolated to zero impurity
Amount of impurity mole fraction	0.0029 ±0.0004	0	0.0034 ±0.0005	0
Boiling point [a] at:				
760 mm °C	234.35 ±0.05	234.35 ±0.05	234.39 ±0.05	
217.2 mm °C	184.98 ±0.05	184.98 ±0.05		
57.3 mm °C	143.76 ±0.07	143.76 ±0.07		
Freezing point in air at 1 atm °C	−23.02 ±0.01	−22.90 ±0.03	−23.04 ±0.01	−22.95 ±0.0
Density [b] at:				
20° C g/ml	0.9720 ±0.0001	0.9720 ±0.0002	0.9720 ±0.0001	
25° C g/ml	.9682 ±0.0001	.9682 ±0.0002	.9683 ±0.0001	
Refractive index [a] at:				
20° C n_C	1.53937 ±0.00005	1.53937 ±0.00010	1.53935 ±0.00005	
20° C n_D	1.54395 ±0.00005	1.54395 ±0.00010	1.54397 ±0.00005	
20° C n_F	1.55536 ±0.00005	1.55536 ±0.00010	1.55527 ±0.00005	
25° C n_C	1.53738 ±0.00005	1.53738 ±0.00010	1.53735 ±0.00005	
25° C n_D	1.54190 ±0.00005	1.54190 ±0.00010	1.54188 ±0.00005	
25° C n_F	1.55325 ±0.00005	1.55325 ±0.00010	1.55324 ±0.00005	
Refractive dispersion at:				
20° C (n_F-n_C)	0.01599 ±0.00005	0.01597 ±0.00005	0.01592 ±0.00005	
25° C (n_F-n_C)	.01587 ±0.00005	.01588 ±0.00005	.01589 ±0.00005	
Specific dispersion at:				
20° C $(n_F-n_C)/d$	.01645 ±0.00005	.01645 ±0.00005	.01638 ±0.00005	
25° C $(n_F-n_C)/d$	.01639 ±0.00005	.01639 ±0.00005	.01641 ±0.00005	

[a] Determined by B. J. Mair with the apparatus of C. B. Willingham and F. D. Rossini.
[b] Determined by the Capacity and Density Section of this Bureau.
[c] Determined by L. W. Tilton, of the Optical Instruments Section of this Bureau.

VI. SUMMARY OF AMOUNTS OF MATERIAL PROCESSED, LOSSES DURING PROCESSING, AND AMOUNTS OF HYDROCARBONS ISOLATED

In table 6 is given a summary of the material processed, the losses during processing, and the amounts of the individual hydrocarbons separated. For an explanation of a similar table, together with a description of the method used in allocating the losses and in computing the percentages of the hydrocarbons isolated, the reader is referred to the preceding publication [1]. The ninth column of table 6 gives the total amount of the given hydrocarbon isolated, and the tenth column gives the total amount of the hydrocarbon estimated to be present in the petroleum. In both columns the values are in percentage, based on the original distillate, 114° to 144° C at 56.8 mm Hg, as 100 percent. There are included in this table values for the amounts of naphthalene in this petroleum taken from the preceding publication [1]. The total amount of the seven aromatic hydrocarbons actually determined to date as individual compounds amounts to 5.32 percent of the distillate from 114° to 144° C at 56.8 mm Hg and 27.8 percent of all the aromatic material in this same distillate. The corresponding values for the total amount of these seven compounds estimated to be present are 5.76 percent and 30.1 percent, respectively.

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TABLE 6.—*Summary of the material processed, losses due to processing, and amounts of hydrocarbons isolated*

Material	Volume	Process	Material lost in process		Product	Amount of the product or of the given hydrocarbons separated	Amount of the hydrocarbon previously separated [1]	Total amount of the given hydrocarbon isolated *	Estimated total amount of the given hydrocarbon in the petroleum
			Volume						
	Liters		*Liters*	*Percent*		Percentage of the distillate 114° to 144° C (at 56.8 mm Hg)	Percentage of the distillate 114° to 144° C (at 56.8 mm Hg)	Percentage of the distillate 114° to 144° C (at 56.8 mm Hg)	Percentage of the distillate 114° to 144° C (at 56.8 mm Hg)
Aromatic distillate (118° to 120.5° C at 56.8 mm Hg).	3.768	Azeotropic distillation and crystallization.	0.824	21.9	1,2,3,4-Tetramethylbenzene	1.01		1.01	1.06±0.07
					5,6,7,8-Tetrahydronaphthalene	0.24		0.24	0.27±0.03
					Unresolved material (high index)	.04			
					Unresolved material (low index)	1.87			
Aromatic distillate (137° to 140° C at 56.8 mm Hg).	2.564	Azeotropic distillation.	.505	19.7	2-Methyl-5,6,7,8-tetrahydronaphthalene.	0.62		.62	.68±0.06
					Unresolved material (high index)	.11			
					Unresolved material (low index)	1.41			
Aromatic distillate (141° to 144° C at 56.8 mm Hg).	2.050	Azeotropic distillation.	.228	11.1	1-Methyl-5,6,7,8-tetrahydronaphthalene..	0.40		.40	.65±0.12
					Unresolved material (high index)	.07			
					Unresolved material (low index)	1.24			
Aromatic distillate (144° to 148° C at 56.8 mm Hg).	1.283	Azeotropic distillation.	.080	6.3	Unresolved material (low index)	0.81			
					2-Methylnaphthalene	.40	1.28	1.80	1.80±0.10
Aromatic distillate (148° to 150° C at 56.8 mm Hg).	0.252				2-Methylnaphthalene	.12			
					1-Methylnaphthalene	.12			
Aromatic distillate (150° to 151° C at 56.8 mm Hg).	.364				1-Methylnaphthalene	.37	0.35	0.84	0.84±0.06
					Naphthalene		.41	.41	.46±0.04

* The losses occurring in each process of fractionation were charged equally on a fractional basis to the products obtained from the given process. In this way, the total materia actually on hand, regardless of the losses which occurred, represent the original distillate 114° to 144° C at 56.8 mm Hg (see reference [1].

VII. PREVIOUS INVESTIGATIONS

Of the four hydrocarbons, 1,2,3,4-tetramethylbenzene, 5,6,7,8-tetrahydronaphthalene, 1-methyl-5,6,7,8-tetrahydronaphthalene, and 2-methyl-5,6,7,8-tetrahydronaphthalene, whose isolation is described here, none, as far as the authors are aware, has been isolated previously from petroleum. However, Nenitzescu, Isacescu, and Isopescu [13], using the aromatic fractions from a Gura Ocnitei oil, concluded, from combustion analyses of fractions which distilled between 204° and 205° C at atmospheric pressure, that these fractions contained 1,2,3,4-tetramethylbenzene. As additional evidence supporting this conclusion, these authors prepared a bromide from these fractions with a melting point which agreed with the melting point of 5,6-dibromo-1,2,3,4-tetramethylbenzene. Ross and Leather [18] treated a fraction of a Borneo oil, which distilled in the neighborhood of 200° C, with fuming nitric acid and obtained a nitro compound which, on the basis of combustion analyses, they believed to be dinitrotetrahydronaphthalene.

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EFFECTS OF HYDROCHLORIC ACID AND SALTS ON THE ABSORPTION OF LIGHT BY β-NAPHTHOQUINONESULFONIC ACID

By Baker Wingfield and S. F. Acree

ABSTRACT

In order to evaluate the effects of hydrochloric acid and neutral salts on the absorption of light by an organic acid dye, spectrophotometric measurements were made of a series of solutions of hydrochloric acid and of neutral salts plus hydrochloric acid, each containing 3×10^{-4} *M* β-naphthoquinonesulfonic acid.

The dye in these solutions showed small differences in spectral absorption. Similar differences may contribute to the changes of absorption shown by true indicators. Most of the data were compatible with the assumption that new absorption bands were not produced or that there was no considerable shift in the position of the original bands with respect to wave number.

The increase in the absorption by the dye in the presence of salts was proportional to the square root of the molar activity of the electrolyte. The proportionality factor was different for each salt and varied from 0.144 to 0.353.

The results suggest that the specific effects of ions on the absorption indices of positive, neutral, and negative forms of an indicator must be taken into account, as well as the normal effects of the ions on the dissociation of the indicator, for accurate pH measurements.

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I. INTRODUCTION

It is well known that intense color changes are produced by the addition of acids or bases to solutions containing organic compounds of certain classes. The color change is associated with the ionization (or suppression of ionization) of one of the acidic or basic groups of these compounds. The spectral absorption is different for their ion and mole forms. Because the relative proportion of ion and mole forms changes with the hydrogen-ion concentration, these compounds are used in pH measurements.

The use of the indicator method [1] for pH measurements presupposes the validity of a generalized mass law equation for the reaction of hydrogen ions with the indicator itself. For a monovalent acid indicator the equation is

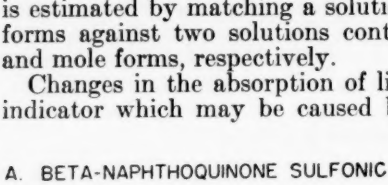
$$K=\frac{[H^+]\,[In^-]\,f_{H^+}f_{In^-}}{[HIn]\,f_{HIn}},$$

[1] See references [1, 2, 4, 5, 9, 14, 19, 21, 24, and 27] for reviews of the theories of indicators and the mass law applications in pH measurements.

where $[H^+]$, $[In^-]$, and $[HIn]$ are the concentrations of hydrogen ion, indicator anion, and undissociated indicator, respectively, f_{H^+}, f_{In^-}, and f_{HIn} are the respective activity coefficients of these components, and K is the ionization constant. It is presumed that $K(f_{HIn}/f_{In^-})$ has been determined. The ratio In^-/HIn which then determines $[H^+]f_{H^+}$ is estimated by matching a solution containing a mixture of the two forms against two solutions containing known amounts of the ion and mole forms, respectively.

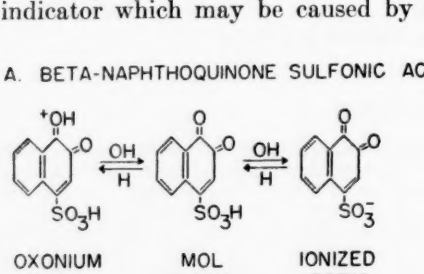
Changes in the absorption of light by either or both forms of the indicator which may be caused by different environments, such as surrounding electric fields [1, 25][2] from electrolytes, are thus excluded from consideration. Such changes in light absorption, if they exist, will affect the color and may lead to incorrect estimates of pH. These optical effects by salts will be termed "specific salt effects" to differentiate them from the normal effect of salts on the activity coefficients of the indicator acid.

A. BETA-NAPHTHOQUINONE SULFONIC ACID.



OXONIUM FORM | MOL FORM | IONIZED FORM

B. SULFONPHTHALEINS



OXONIUM FORM | MONOVALENT FORM | DIVALENT FORM

FIGURE 1.—*Various forms of β-naphthoquinonesulfonic acid and sulfonephthaleins.*

It is easier to estimate the magnitude of specific salt effects on the different colored forms of indicators, if work is begun with a substance related in its chemical structure to many of the useful indicators, but which is not an indicator itself and therefore does not exhibit intense color changes with ionization. Such a substance is found in β-naphthoquinonesulfonic acid, which contains a quinone chromophore and a sulfonate group and possesses the typical yellow color of a sulfonephthalein free acid. (See fig. 1.)

The purpose of this work is therefore to determine how the addition of salts or the further additions of acid to acid solutions of β-naphthoquinonesulfonic acid affects the molar absorption indices[3] of this compound.

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[2] Figures in brackets indicate the literature references at the end of this paper.

[3] The molar absorption index, k, which will be referred to in the remainder of the paper as molar index, is $\log(100/t)$, where t is the calculated transmittancy in percent when the concentration of the absorbing material is 1 mole per liter and the length of the absorbing path is 1 cm. This is a constant for a particular substance and wavelength, provided Beer's law holds. The molar absorption index is obtained from actual transmittancy data from the expression $[\log(100/T)]/cl$, where T is the measured transmittancy in percent, c is the concentration of the dye in moles per liter, and l is the length in centimeters. In calculations involving both the concentration and the absorption, it is necessary to use the molar absorption index.

II. EQUIPMENT AND CHEMICALS

A Keuffel and Esser visual spectrophotometer, modified with variable slits in both eyepiece and collimator ends, was used for the preliminary investigations on solutions of β-naphthoquinonesulfonic acid. A General Electric recording spectrophotometer of the Hardy type, which has been discussed by Hardy [10] and Michaelson [18], was used to secure the precision curves of the transmittancies of the various dye solutions. This instrument was fitted with slits of a width which transmitted a spectrum region of approximately 4 mμ. The recorded transmittancies, which covered the spectral region from 400 to 750 mμ, could be read to 0.1 percent of full scale. A few measurements were made with a Coleman photoelectric spectrophotometer fitted with slits of a width which transmitted a spectrum region of approximately 5mμ. The transmittancies could be measured from 350 to 1,000 mμ with this instrument and were read to 0.1 percent.

The pair of transmission cells used with the Keuffel & Esser and the General Electric recording instrument were constructed of Pyrex glass. The ends of glass tubing, 2.5 cm in diameter, were ground and polished to give a length of 2.000 cm. Cells of 5-cm length were also used. Circular disks of selected Pyrex glass, slightly larger in diameter than the tubing, were ground and polished to a uniform thickness of approximately 2 mm. These disks were then fused to the ends of the prepared tubes. A glass side tube had been previously sealed into the glass tubes for filling and emptying the cells. The Coleman spectrophotometer was supplied with two matched glass cells having plain, parallel walls which interposed a liquid column of approximately 1.3 cm in the light path.

Commercially prepared sodium β-naphthoquinonesulfonate was repurified once by the method of Folin [7], and was stored in lightproof bottles under anhydrous conditions. The dye, dissolved in water, fades slowly when it is exposed to strong light. In acid solutions, however, the dye proved sufficiently stable for spectrophotometric measurements. Tests showed that no fading could be observed in the presence of 0.005 *M* HCl during the time elapsing between the preparation of the solution and the measurement of the transmittancy in the visible spectrum. A stock solution of the dye in 0.05 *M* HCl was prepared and allowed to stand in dim light. Samples taken from this solution immediately after preparation, and at various intervals up to 6 hours, were diluted to 0.005 *M* HCl. The transmittancy values for these solutions did not differ from one another in excess of the experimental error. In alkaline solutions the dye deteriorates, as shown by a darkening of its color. To determine whether a slow change takes place in acid solutions similar to that occurring in basic solutions (but visible only in alkaline solutions), transmittancy measurements were made on solutions of the dye prepared from the above stock acid solution after adjusting it to pH 8. The transmittancy measurements indicated that the acid stock solution had not suffered any appreciable deterioration in 6 hours. Definite changes in the absorption by the dye occurred during 24 hours in both the acidic and basic solutions.

The dye solutions were prepared for transmittancy measurements in the following manner: 78.1 ±0.1 mg of the solid sodium β-naph-

thoquinone sulfonate was dissolved in 25 ml of 0.2 *M* HCl and diluted at once to 100 ml. This solution was freshly prepared for each day's run. A 10-ml portion of the concentrated dye solution was then transferred to a 100-ml volumetric flask, the desired amount of concentrated salt solution added, and the solution diluted to the mark. The final solution was then 0.0003 *M* in the dye, 0.0003 *M* in sodium ion, and 0.005 *M* in HCl, plus the salt. This procedure was followed for KCl, Li_2SO_4, and $CaCl_2$. In the solutions in which HCl was present alone, sufficient acid was added to obtain the desired concentration. In the preparation of the $AlCl_3$ solutions, the final concentration of HCl was adjusted to 0.15 *M* to prevent hydrolysis of the salt. At the same time that the dye solutions were prepared for use in one cell, solutions for the companion cell were made in which the dye was omitted but which were identical in regard to the other components. The recorded transmittancies were dependent upon the dye alone, since any absorption or reflection by the salt, acid, or glass was balanced by a similar loss in the other cell. The solutions were prepared and the measurements made at room temperature, about 20° to 25° C.

The salts used were chemically pure grades. The only treatment given them was a filtration of the concentrated solutions.

III. EXPERIMENTAL PROCEDURE

The portion of the single absorption band used in the following computations extended from wave numbers[4] of about 20,000 to 23,260 (500 to 430 mμ). Figure 2 is typical of the spectrophotometric data. The ordinates of the recorded curves were read at 10-mμ intervals and corrected to percentage transmittancy according to the methods outlined by Gibson and Keegan [8]. The accuracy of the transmittancy measurements was of the order of 0.5 percent of full scale. These transmittancies were used to calculate the molar indices. These indices were plotted against wave number. The smooth curves drawn through these points are shown in figures 3 to 6. The curve for the $AlCl_3$ solutions is omitted to conserve space.

The solid portions of the curves represent the more valuable part of the data; in the dotted portions, the data are less certain, because the values of the molar indices are too small to be useful (wave numbers 18 to 20×10^3) and the experimental transmittancy data are too unreliable (wave numbers 23 to 25×10^3).

Since the changes in the molar indices were to be used as measures of the effect of HCl and of the salts on the dye, the constancy of the ratio of the molar indices of any two curves at identical wavelengths was determined at intervals of 10mμ. For concentrations of acid or salt up to 0.5 *M*, the index ratios for any two curves[5] were found to be constant within the experimental error. At salt or acid concentrations of 1 or 2 *M*, the ratios showed inconsistencies which were equivalent to transmittancy variations of 0.6 to 1.4 percent. For the dye in $CaCl_2$ solutions, inconsistencies in the ratios of individual curves to the 0.005 *M* HCl curve varied from values equivalent to 0.8 percent

[4] "Wave number" in this paper is defined as the number of wavelengths in a centimeter.

[5] In these calculations, each individual curve was compared with the curve for the dye in 0.005 *M* HCl, so that all of the changes were related to the molar index values for the dye under these conditions. The average ratio for each curve compared with that for 0.005 *M* HCl increased with increase in concentration for each electrolyte.

in transmittancy at $CaCl_2$ concentrations of 0.005 and 0.1 *M*, to 6 percent at 2 *M*.

The constancy of the ratios of the molar indices between any two curves at identical wave numbers up to 0.5 *M* electrolyte, the absence of any considerable shift in the band with respect to wave number,

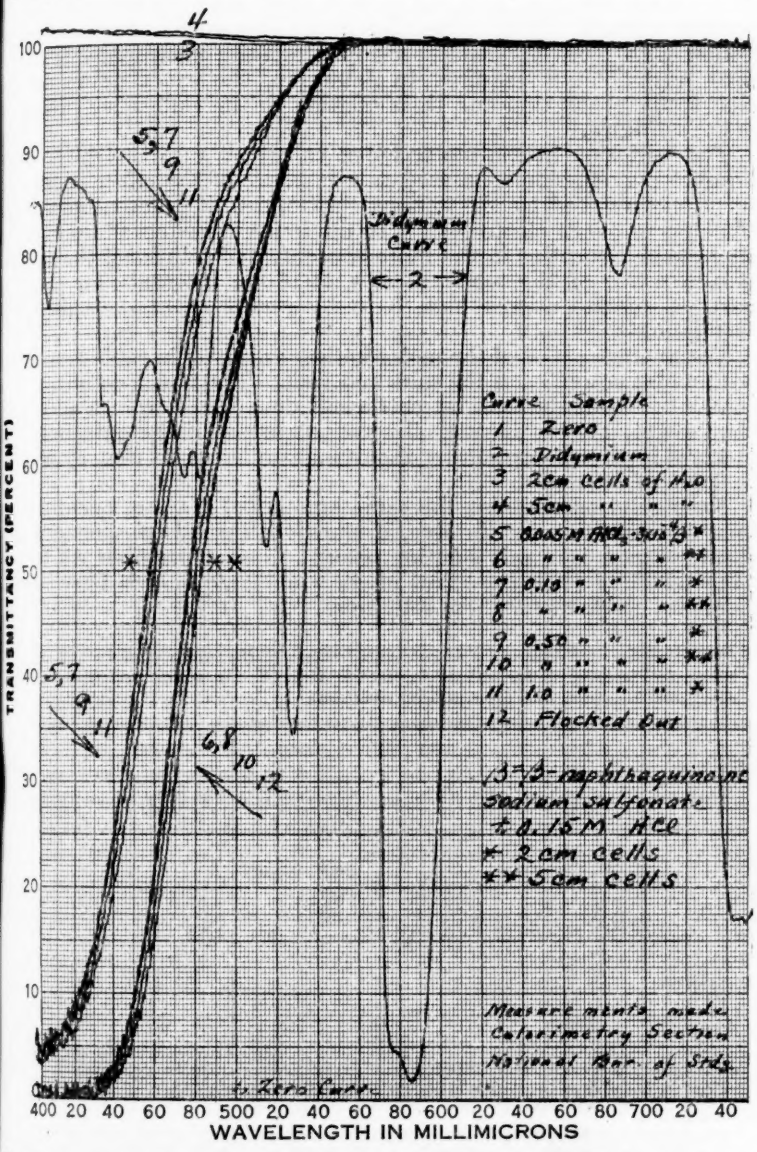

TRANSMITTANCY (PERCENT)
WAVELENGTH IN MILLIMICRONS
Didymium Curve
Curve Sample
1 Zero
2 Didymium
3 2cm cells of H2O
4 5cm " " "
5 0.005 M HCl-3% β
6 " " " " **
7 0.10 " " " *
8 " " " " **
9 0.50 " " " *
10 " " " " **
11 1.0 " " " *
12 Flocked Out
β-naphthaquinone Sodium Sulfonate + 0.15 M HCl
* 2cm cells
** 5cm cells
Measurements made Colorimetry Section National Bur. of Stds.
to Zero Curve

FIGURE 2.—*Transmittancy of 0.0003 M β-naphthoquinonesulfonic acid in 0.15 M* HCl *plus 0.005 M to 1 M* $AlCl_3$ *in 2- and 5-cm cells.*

This is a facsimile of the laboratory record.

and the apparent general increase in absorption at all wave numbers in the ultraviolet[6] and visible with increased concentration of electrolyte, indicate that the effect of electrolytes on the absorption band (peak 26,500 wave number) is mainly a uniform increase in index at all wave numbers. There is, however, some flattening at the peak for high concentrations, and indications of a slight broadening of the band or a small shift in its position in the spectrum. Further investigation with more accurate spectrophotometric measurements in the near ultraviolet is required to determine the exact nature of the changes in absorption and their relation to the colligative properties of the solutions.

The variation in the molar index values at any convenient wave number may therefore be used as a measure of the effect on the absorption produced by the various electrolytes at different concentrations up to 0.5 *M* electrolyte. To minimize the effect of nonuniform changes in absorption in the more concentrated solutions, the average of the ratios of the molar indices, at 10 mμ intervals, for the solid portions of the curves (figs. 3 to 6) were used in the subsequent correlations.

The average ratios of the molar indices are given in table 1, together with molar activities of the salts and HCl. The molar activities were calculated from the activity coefficient data taken from a number of sources [11, 12, 17, 22, 23]. In the treatment of the data, all of the changes in the absorption by the dye are referred to that by the dye in 0.005 *M* HCl.

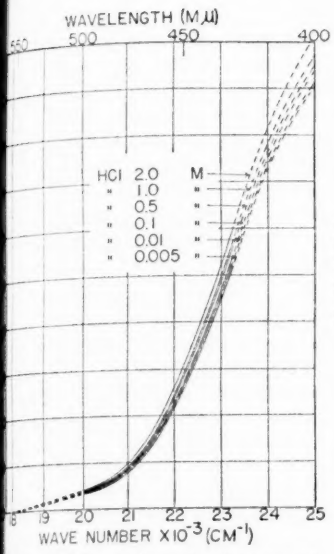
Each solution contains the same amount of Na ion, and its effect on the absorption by the dye, if additive, can be considered a constant. Since each salt solution, except those containing $AlCl_3$, contains 0.005 *M* HCl, the effect of the stabilizing acid is likewise considered a constant for these solutions.

TABLE 1.—*Average observed and calculated ratios of the molar indices (10-mμ intervals) with respect to the values for 0.005 M* HCl, *the molar activities,*[a] *M*±, *of* HCl *and the salts, and the equation constants*

Molar concentration of solute	HCl			KCl			Li_2SO_4			$CaCl_2$			$AlCl_3$		
	Obs. ratio	Calc. ratio	*M*±	Obs. ratio	Calc. ratio	*M*±[b]	Obs. ratio	Calc. ratio	*M*±[b]	Obs. ratio	Calc. ratio	*M*±[b]	Obs. ratio	Calc. ratio	*M*±
0.005	1.000	1.024	0.0046	0.990	0.989	0.0046	.....	.....	.....	1.084	1.038	0.0063	1.012	0.997	0.00
0.01	1.033	1.028	.0091	.....	.....	.....	1.015	1.009	0.011	.....	.....	.....	.....	.....	.....
0.1	1.058	1.055	.080	[c]1.024	[c]1.020	[c].074	.....	.....	.....	[c]1.111	[c]1.112	[c].083	1.029	1.050	.07
0.5	1.097	1.104	.388	1.059	1.067	.330	1.056	1.073	.305	1.193	1.236	.409	1.132	1.137	.34
1.0	1.140	1.132	.826	1.097	1.110	.623	1.109	1.098	.497	1.371	1.394	1.181	1.264	1.264	1.11
2.0	1.214	1.223	2.106	1.154	1.149	1.212	.....	.....	.....	1.843	1.820	5.267	.....	.....	.....
Equation constants:															
Intercept		1.014			0.978			0.993			1.010			0.978	
Slope		0.144			.155			.149			0.353			.271	

[a] The activity coefficients were interpolated from data in the literature [11, 12, 17, 22, 23].
[b] These molar activities do not include the small amounts of stabilizing HCl.
[c] These ratios and molar activities are for 0.095 *M* salt concentration.

[6] Solutions of the dye in 0.005 *M* HCl, in 2 *M* HCl, and in 2 *M* $CaCl_2$+0.005 *M* HCl were also studied with the Coleman regional spectrophotometer at 350 to 1,000 mμ and with the type E1 Hilger spectrograph at 200 to 800 mμ. The dye gives three bands with peaks at approximately 26,500 (377 mμ), 35,000 (286 mμ), and 39,000 (257 mμ) wave numbers, with no indication of absorption from 550 to 1,000 mμ. In saturated HCl there was no change in color indicating the formation of a new band such as those characterizing the sulfonephthalein oxonium salts in concentrated HCl.



RE 3.—*Molar index of solutions of naphthoquinonesulfonic acid in* HCl *tted against wave numbers.*

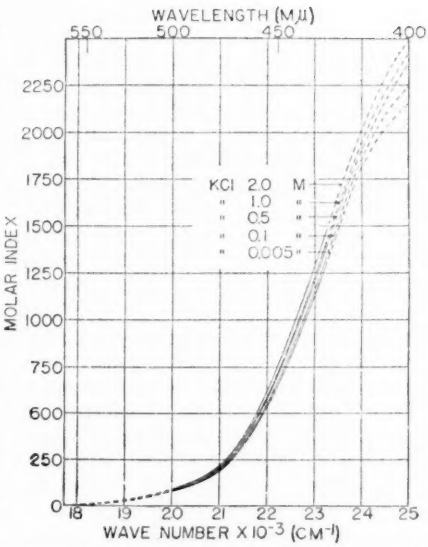
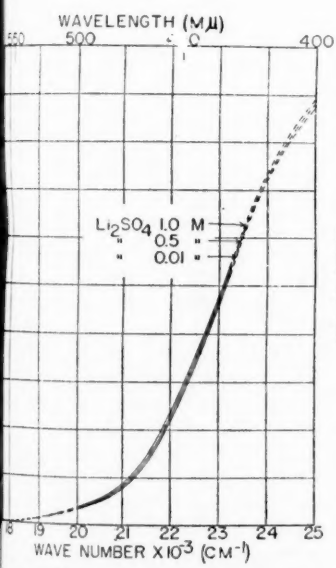


FIGURE 4.—*Molar index of solutions of β-naphthoquinonesulfonic acid in* KCl *plotted against wave numbers.*



RE 5.—*Molar index of solutions of naphthoquinonesulfonic acid in* Li_2SO_4 *tted against wave numbers.*

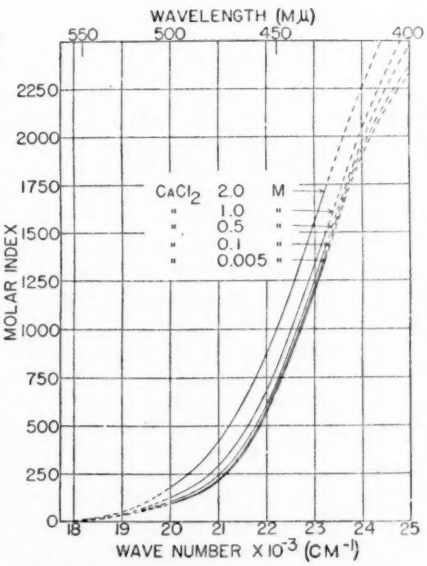


FIGURE 6.—*Molar index of solutions of β-naphthoquinonesulfonic acid in* $CaCl_2$ *plotted against wave numbers.*

IV. DISCUSSION

In the use of spectral absorption by indicators in pH measurements, it is usual to treat the measured molar index at any particular wave number as the sum of two values. These are the products of the individual molar index values of the ionized and nonionized forms of the indicator chromophore and their respective percentages. The $-SO_3H$ group, however, is highly ionized, so the presumption is raised that the measured molar index is that characterizing the ionized form only. To test this assumption a comprehensive analysis was made of the absorption data in relation to the mean molar activities, ionic strength, and concentrations of the solutions. A number of reasonable (high) values for the ion-to-mole ratios and ionization constant of the $-SO_3H$ group were used. The results showed that the changes in molar index ratio cannot be readily explained in terms of these factors unless the improbable assumption is made that HCl differs from all the other electrolytes in having no specific effect on the dye. On the other hand, on the predication that the $-SO_3H$ group is practically 100 percent ionized and that the ratio of its ions and moles plays no appreciable part in the observed changes in absorption, the specific salt effect appears to be approximately proportional to the square root of the mean molar activity of each electrolyte investigated.

The best empirical expression relating the molar index ratio and activity for each electrolyte was found to be $y=a+bx$, where y is the molar index ratio, x is the square root of the activity of the salt or acid, b is the slope of the curve, and a is the molar index ratio at zero salt concentration. In table 1 are given the observed and calculated molar index ratios and the constants for each salt. An experimental error of 0.5 percent of full scale in the transmission values would correspond to 0.026 in the average index ratio. The table shows that all of the calculated values lie within this error with the exception of 2 points (0.005 M and 0.5 M $CaCl_2$). The a values, with a maximum difference of 0.036, are in fair agreement. Definite conclusions cannot be drawn regarding the calculated and observed values of the molar index ratios of the dye in $AlCl_3$. No account has been taken of the larger amount of HCl in these solutions than that in the reference conditions of the dye in 0.005 M HCl. If the reference conditions were taken as the dye in 0.15 M HCl, a for $AlCl_3$ should be approximately 1.064. This would cause the data to depart by several percent from the linear relationship found for other salts. At present no explanation can be offered for this effect.

The maximum change in the molar index of the dye, from dilute to concentrated solutions of electrolytes, was approximately 84 percent of the index for 0.005 M HCl. This change is much less than is found at any given wavelength near the peak of the absorption band for sulfonic acid indicators, such as bromthymol blue or metacresol purple, when they are converted from the free acid form to the highly colored, dibasic ions in acid and alkaline solutions. These indicators show a rise of sevenfold to eightfold in their molar indices, in the change from mole to ion form, in the spectral region of the absorption band for each indicator in its yellow form. Thus the maximum effect on the absorption by β-naphthoquinonesulfonic acid is less than 15 percent of the effect of H-ions on the absorption by similar forms of indicators.

The data show that increase in absorption by the dye is the direct physical result of the presence of increasing amounts of strong electrolytes, rather than the result of the effect of the added ions on the ionization of the dye, and is specific for each salt [3]. This is analogous to the specific cationic effect on the light absorption by nitrate ions reported by von Halban and Eisenbrand [26]. The relationship of the molar activity of the solution to the absorption by the dye is consistent with the views held by von Halban and Ebert and others [1, 25] that the electrostatic forces between ions may be largely responsible for the observed changes.

Rabinowitch and Epstein [20] have recently shown that the effect of 1 *M* KCl on thionine in water is to reduce its absorption index by approximately 20 percent. As shown in table 1, 1 *M* KCl changes the absorption by about 10 percent in the opposite direction. It is of interest to note that the two compounds being compared were in oppositely charged ionic forms.

It is not unreasonable to presume that the absorption of light by all indicators containing a quinonesulfonate grouping will be altered by a specific salt effect in the presence of an electrolyte. This modification of the absorption may introduce errors in pH estimations made with indicators when it is assumed that measurements of absorption or hue give directly the In^-/HIn ratio, which is a function of pH. If the specific salt effect has the same magnitude for the In^- and HIn or other [6] forms of the indicator involved in eq 1, the resulting compensation leaves the pH values unaffected by this factor.

V. CONCLUSIONS

1. The absorption index of β-naphthoquinonesulfonate ion is increased by HCl and salts in proportion, approximately, to the square root of their activities.

2. Hydrochloric acid acts in the same way as a salt on the absorption of light by the dye.

3. The molar indices of the β-naphthoquinonesulfonate ion in solutions of HCl and salts indicate that the magnitude of the color changes is determined by the specific ions and not by the salt type (uni-uni, uni-di, etc.).

4. The change in the average molar index ratio produced by salts and HCl in concentrations greater than 0.005 *M* is primarily a small increase in magnitude without a marked shift in the absorption band. These optical effects may be due mainly to the influence of the adjacent ions and electric field on the electronic structure and resonance of the quinone group.

5. The evidence of a specific salt effect on the absorbing system of the β-naphthoquinonesulfonate ion points strongly to the possibility that electrolytes may have a similar effect on all indicators and may introduce errors in pH measurements in concentrated solutions.

6. It is concluded that the specific effects of ions on the absorption indices of positive, neutral, and negative forms of an indicator should be investigated, as well as the normal effects of the electrolytes on the dissociation of the indicator, for accurate pH measurements.

The authors express their appreciation to K. S. Gibson, of the Photometry and Colorimetry Section ot the National Bureau of Standards, for advice and the use of the recording spectrophotometer and to H. J. Keegan of that Section for his cooperation in making the transmittancy measurements.

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THERMAL EXPANSION STUDIES OF BORIC OXIDE GLASS AND OF CRYSTALLINE BORIC OXIDE

By James J. Donoghue [1] and Donald Hubbard

ABSTRACT

The expansion characteristics of a boric oxide (B_2O_3) glass and of a sample of crystalline boric oxide have been studied by the interferometer method. The results obtained are chiefly of qualitative interest, but offer a satisfactory picture of some of the difficulties that must be overcome if true expansion data are to be obtained on these materials.

The characteristics of the expansion curves for boric oxide glass and crystalline boric oxide are very different. The sample of crystalline boric oxide had a melting temperature between 450° and 451° C. Upon being heated to its melting point, this material does not recrystallize on cooling, but remains in a fused state, as indicated by the "critical" and "softening" temperatures shown by its expansion curve.

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I. INTRODUCTION

In a study of the physical properties of experimental glasses of the binary systems SiO_2-B_2O_3 and Al_2O_3-B_2O_3, it became desirable to know the coefficient of linear expansion and other characteristics of the expansion curve for the one-component boric oxide (B_2O_3) glass. Published data on the expansion of this glass are highly conflicting, as shown in the review of the subject by Morey [1].[2] Furthermore, with a sample of crystalline boric oxide available, it seemed of interest to make a comparison of the expansion characteristics of the vitreous and crystalline forms of this oxide.

II. PREPARATION OF MATERIALS

The boric oxide glass was prepared by C. A. Faick at 1,050° C in a platinum crucible from boric acid which had passed the American Chemical Society specification for purity [2]. The sample of crystalline boric oxide was donated by S. R. Scholes, of the New York State College of Ceramics, and had been prepared by the method discovered by L. McCullock [3].

[1] James J. Donoghue collaborated in this study before he left the National Bureau of Standards in June 1940.

[2] Figures in brackets indicate the literature references at the end of this paper.

III. EXPERIMENTAL PROCEDURE

The expansion determinations were made by means of the modified Fizeau-Pulfrich interference method [4, 5, 6], using a heating rate of approximately 3°C per minute. The temperature was followed with a Chromel-Alumel thermocouple, calibrated against a small quartz "refraction thermometer" [6, p. 192–194] placed in the position normally occupied by the specimens. This does much to eliminate the temperature error caused by the relatively large gradient between the positions occupied by the thermocouple and that by the specimens, which is so characteristic of a vertical tube furnace [6].

The expansion specimens for the boric oxide glass were drawn from the molten mass by means of a three-tined fork of ⅛-inch Nichrome wire. The glass which adheres to the points when the fork is withdrawn gives small hollow cones which can be shaped into expansion specimens with a minimum amount of grinding and handling [7]. For the crystalline boric oxide, triangular expansion specimens approximately 5 mm high were dry-ground from small pieces broken from the solid mass.

IV. DATA AND RESULTS

1. BORIC OXIDE GLASS

Curve *A* of figure 1 shows the expansion obtained for the initial determination on the drawn specimens of boric oxide glass when heated beyond the annealing temperature, but not to the softening point. This curve has two regions of negative expansion; the one near 150°C is relatively small, while that at the higher temperature is large. Since the specimens were air-quenched from the temperature of the melt, the negative expansion with the minimum near 265°C in the annealing range was to be expected [4, p. 473–475; 8]. Upon cooling these specimens in the furnace from 320°C, which is well above the annealing temperature for this glass, to room temperature, the expansion determination made on the following day showed that the small negative expansion near 150°C still persisted, although altered in position and magnitude, while the large negative expansion of the specimens in the "quenched condition" had been eliminated and in its place was a very large positive expansion, curve *B*, figure 1.

Since anhydrous boric oxide is classified as a dehydrating agent [9], it seemed probable that the irregular negative expansion of the boric oxide glass in the vicinity of 150° C is the result of decomposition of boric acid formed on the surface of the specimens by the reaction of the boric oxide glass with atmospheric moisture. To establish definitely whether this negative expansion was associated with moisture, a series of expansion determinations was made on a set of specimens of the boric oxide glass which had remained in a desiccator over KOH for several weeks. The results are plotted in figure 2 with the segments of the curves near 150° C displaced sufficiently along the ordinates to show the characteristic of each curve. Curve *A* shows a slight rounding off toward a decreasing slope just prior to the negative expansion near 150° C. The data plotted in *B* were obtained by cooling the furnace without disturbing the interferometer set-up of determination *A*, and holding for 1 hour at about 110° C to maintain

a very low relative humidity and to prevent reabsorption of moisture. Upon reheating through 150° C no indication of a negative expansion was found. However, upon cooling to room temperature, again without disturbing the interferometer set-up, and allowing to stand for 24 hours before making another determination, a small negative expansion reappeared (curved *C*). The top curve, *D*, was obtained after placing the specimens in a closed space over water for 24 hours. The resulting

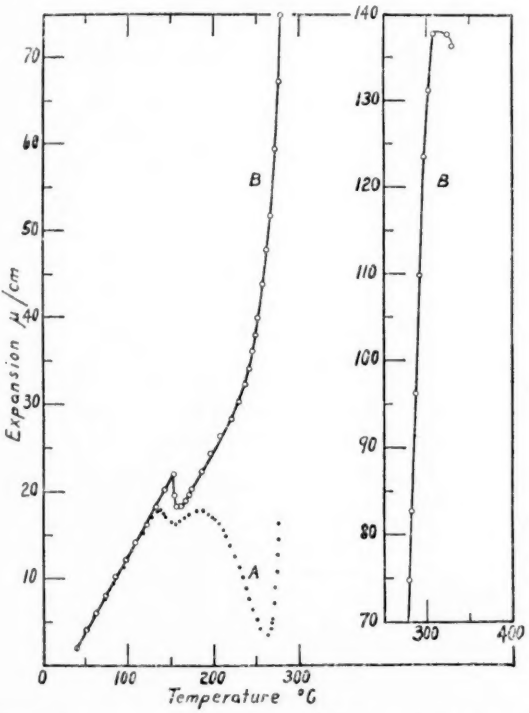

FIGURE 1.—*Expansion curves A and B of fused* B_2O_3, *with the glass in the quenched and annealed conditions, respectively, both determinations exhibiting a negative expansion near 150° C.*

negative expansion was very large. After following the dimensional change for more than 43 microns per centimeter, the passage of the bands became so rapid that no further counts could be made.

The fact that curve *B* passed through the temperature region near 150° C without deflection leads one to believe that a curve closely approximating the true expansion of boric oxide glass could be obtained. However, in light of the knowledge of the tenacity with which boric oxide holds to the final fraction of water, one should hesitate to accept the data as giving the true expansion for B_2O_3 glass.

The two examples of negative expansion shown in figure 1 probably account for most of the discrepancies in the published data. In obtaining a true expansion curve for boric oxide glass, the negative expansion near 150° C presents a more difficult problem to surmount

than does the annealing, because exposure to moisture of the atmosphere while preparing the specimens and making the interferometer set-up must necessarily give rise to some surface contamination. This contaminated surface does not give up all of its water below red

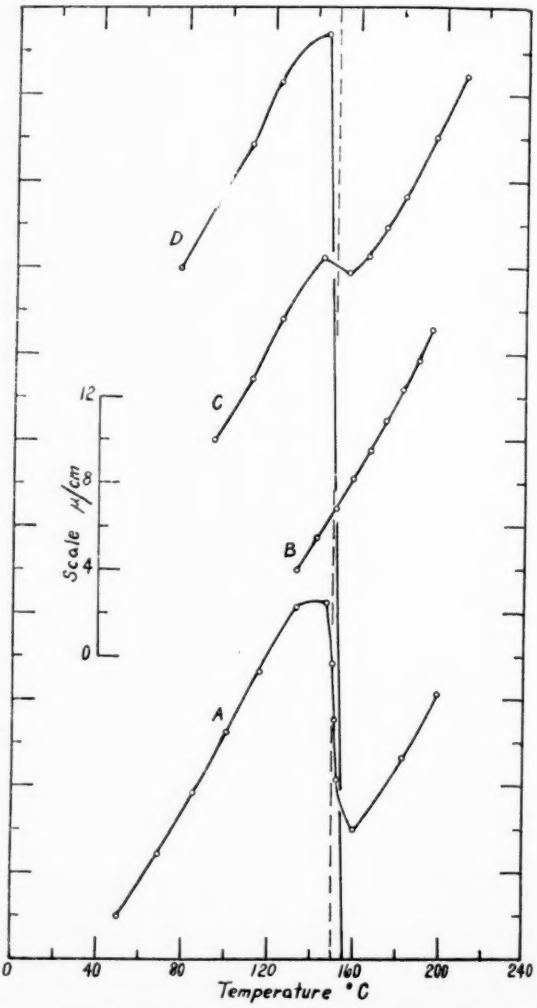

FIGURE 2.—*Expansion determinations of B_2O_3 glass, showing the effect of moistur on the expansion curve near 150° C.*

A, Initial set-up; *B*, after preheating above 170° C and cooling to 110° C; *C*, after cooling to room temperatu and allowing to stand in the furnace 24 hours; *D*, effect of exposing specimens to high humidity for 2 hours.

heat, which is several hundred degrees above the softening temperature of the boric oxide glass. Thus, the specimens cannot be completely freed of moisture without destroying the interferometer set-up.

The difficulty may be better appreciated by following what happens to the boric acid upon heating. According to the older reports

H_3BO_3 gives up water gradually between 80° and 108° C, presumably according to the equation

$$H_3BO_3 = HBO_2 + H_2O, \qquad [10, 11]$$

while between the temperatures 140° to 160° C HBO_2 and H_3BO_3 give up water rapidly to form tetraboric acid.

$$4HBO_2 = H_2B_4O_7 + H_2O$$
$$4H_3BO_3 = H_2B_4O_7 + 5H_2O \qquad [12, 13].$$

If these three reactions were true, they would adequately account for the expansion curve near 150° C. However, a truer picture of what is occurring in this temperature region can be obtained by a careful study of the phase-equilibrium diagram of the system water–boric oxide [14], in which $H_2B_4O_7$ is shown to be nonexistent. In their publication Kracek, Morey, and Merwin report that, upon raising the temperature above 150° C, dehydration continues, yielding a highly viscous liquid whose composition lies between HBO_2 and B_2O_3. This gives rise to the break in the expansion curve which is so conspicuous between 145° and 160° C. Unfortunately, the last of the water is not given up until after the softening temperature of boric oxide glass is reached. As a result, one cannot obtain by the interferometer method (as normally used) the true expansion of boric oxide glass alone, but a composite curve for boric oxide plus an indefinite mixture depending on the quantity of water absorbed by the glass during the period required to make and set up the specimens.

2. CRYSTALLINE BORIC OXIDE

A similar difficulty is encountered in determining the expansion of crystalline boric oxide by the interferometer method. The expansion curve in figure 3 obtained for the sample of crystalline boric oxide shows the presence of a slight negative expansion between 155° and 161° C. and a melting point at 450.8° C. The effect near 160° C is probably due to moisture, but it must also be noted that this is unmistakably at a higher temperature than the moisture effect given by the boric oxide glass, and that this higher temperature corresponds very closely to the lowest eutectic temperature of 158.5° C between H_3BO_3 and HBO_2 III [14, p. 171].

One feels justified in accepting the range 450° to 451° C as a melting temperature because immediately thereafter the bands rushed by very rapidly instead of slowly, as is so characteristic of the softening temperature of a glass. Coincident with the melting temperature, the deformation of the interference bands near the base of the pegs indicated severe attack on the quartz interferometer flats. After cooling to room temperature, the pegs were securely fused to both the upper and lower plates. The value of 450.8° C obtained for the melting temperature of the crystalline boric oxide, although in good agreement with the value of 450° ±2° C reported by Kracek, Morey, and Merwin [14], may be somewhat low because of the possible presence of water, fused B_2O_3, or HBO_2 III as an impurity. That some impurity is present is indicated by a "bulge" in the expansion curve (fig. 4) for peg specimens which had been preheated well above 150° C to eliminate moisture. This bulge, which persisted after three passages through this temperature range, reached a maximum at 200° C. Furthermore, petrographic inspection by H. Insley of the original

sample revealed that not all of the specimen was in the crystalline state. Therefore, the curve in figure 4 must not be considered the true expansion curve for crystalline boric oxide. However, the melting point obtained is near that reported by Kracek, Morey, and Merwin

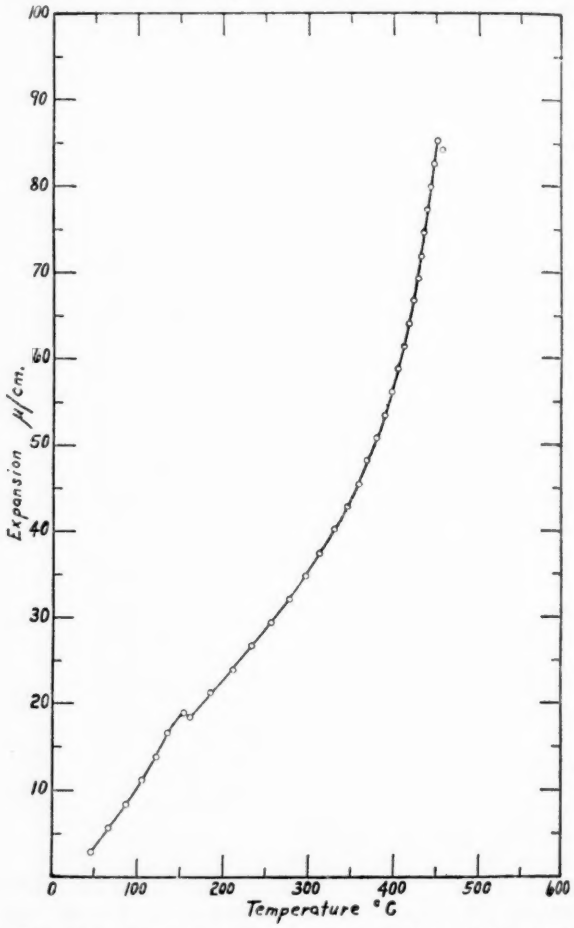

FIGURE 3.—*Expansion curve for a sample of crystalline* B_2O_3, *showing a small negative expansion between 155° and 161° C.*

but appreciably lower than the lower limit of the range 460° to 470° C reported by L. McCulloch [3].

The melting point of the crystalline material prepared by Scholes is not to be associated with the temperature of 294° C reported for supposedly crystalline B_2O_3 by Cole and Taylor [15]. Disregarding all other possibilities, the value of 294° C, obtained with the differential thermocouple, can be adequately accounted for by the large heat absorption which must accompany the large volume change indicated by the long neck of the expansion curve of boric oxide glass (*B*, fig. 1). Since the region of maximum volume change should be the temperature of maximum heat absorption, the temperature obtained by the differ-

ential thermocouple should be that indicated by the first derivative of the expansion curve. Plotting $\Delta E/\Delta T$ of the data for figure 1 against T, one obtains a curve which has a complete reversal between 285° and 295° C, with a sudden decline beginning at 293° to 294° C (fig. 5).

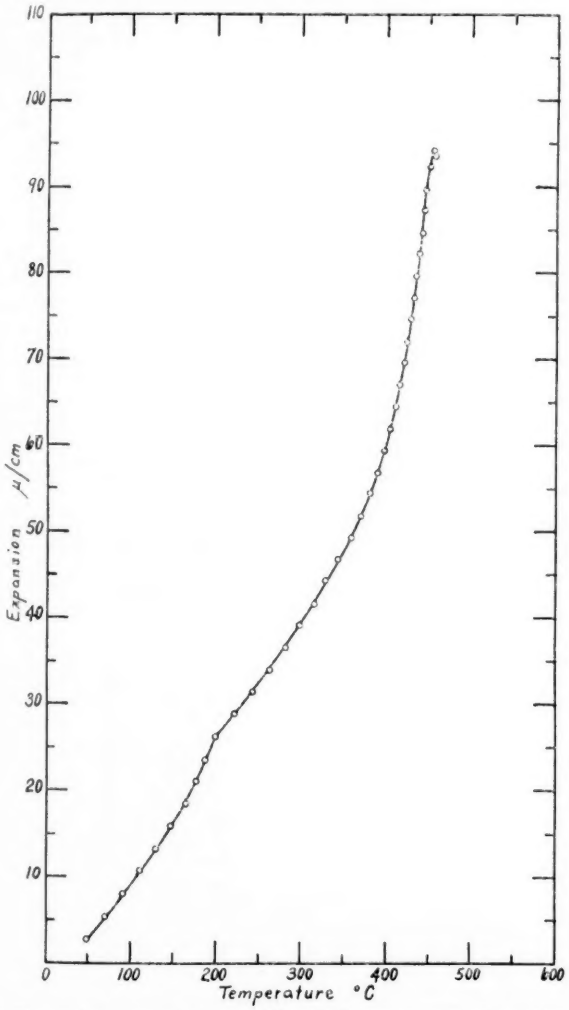

FIGURE 4.—*Expansion curve for crystalline* B_2O_3 *after preheating above 150° C to remove moisture.*

The "bulge" can probably be accredited to the presence of some noncrystalline B_2O_3.

The correspondence is sufficiently close to leave little or no doubt that the temperature recorded by Cole and Taylor as the melting point of their supposedly crystalline boric oxide, and obtained by the differential thermocouple, is the region of the endothermic reaction accompanying the rapid expansion of fused boric oxide.

Another interesting observation is, that after crystalline boric oxide has once been heated to the melting point, additional deter-

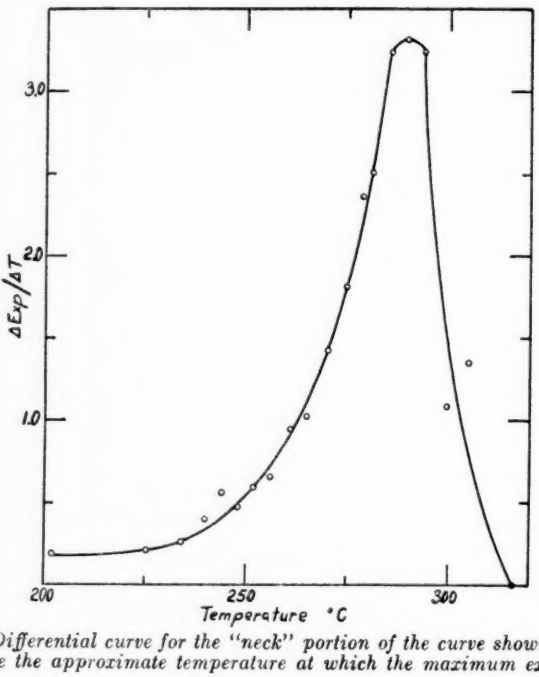

FIGURE 5.—*Differential curve for the "neck" portion of the curve shown in figure 1, to determine the approximate temperature at which the maximum expansion rate occurs.*

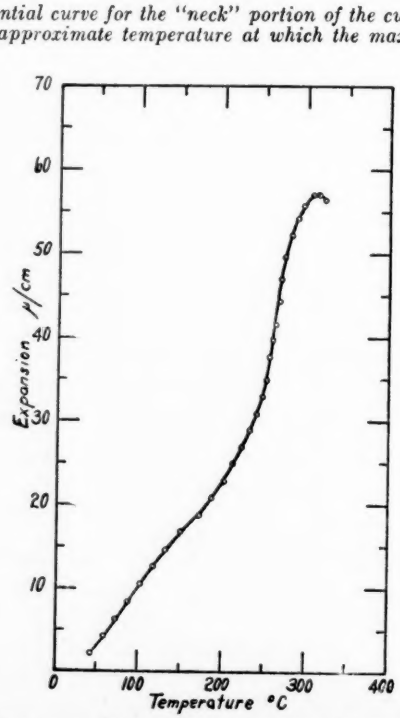

FIGURE 6.—*Expansion curve obtained after specimens of crystalline* B_2O_3 *had been heated to the melting temperature.*

minations of its expansion show that it has taken on some of the characteristics of boric oxide glass, with a softening temperature at 315° C and a critical temperature near 235° C. (Compare curve in fig. 6 with curve *B* of fig. 1.)

V. CONCLUSIONS

Although carefully controlled expansion measurements have been made by the interferometer method on a boric oxide glass and a sample of crystalline boric oxide, no quantitative values are offered for the coefficient of expansion for these materials, because the results indicate definitely that the true expansion curves have not been obtained.

For the boric oxide glass it has been shown that moisture vitiates the results and that moisture, having once been absorbed by the glass while preparing and setting up the specimens, cannot be entirely removed except at temperatures far above the softening point of the boric oxide glass. From this it is evident that the interferometer method as normally used is incapable of giving correct values for the expansion of this material. Better results could be expected by using a bar specimen of the glass and following the procedure of Souder and Hidnert [16]. By their procedure the effect produced by the surface condition of the specimen would be greatly minimized. Also, good results might be expected from the use of a liquid dilatometer of the Spaght and Parks type [17], provided one could be designed that could be heated and exhausted at a temperature near 1,000° C.

In the case of the crystalline boric oxide it is believed that the curves obtained represent significant deviations from those of the true expansions because of the presence of impurities as well as of moisture.

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WASHINGTON, August 8, 1941.

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TITRATION AND CONDUCTIVITY MEASUREMENTS OF AQUEOUS EXTRACTS FROM BOTTLES

By Edgar H. Hamilton and Donald Hubbard

ABSTRACT

In a study of the titration of aqueous extracts from glass containers, it was shown that certain precautions must be observed if reliable results are to be obtained. "Direct" and "back" titrations were made potentiometrically and with a series of indicators to demonstrate the effect of the presence of CO_2 and of "flakes."

When the alkalinities of the aqueous extracts from bottles, as determined by direct titration, were plotted against their specific conductivities, a linear relation was obtained for 9 out of 13 different bottles. The "back titers" of the filtered extracts, when plotted against the conductivities, gave a similar straight line for the same 9 bottles. The relation between the "back titers" and the conductivities of unfiltered extracts was variable. The results indicate that the determination of only one property of the extracts, such as alkalinity or conductivity, may lead to erroneous conclusions.

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I. INTRODUCTION

Many liquids upon storage in glass containers have been known, at times, to undergo unexpected and undesirable changes in appearance, odor, composition, and alkalinity. Beverages have developed "flakes" high in silica content, which are objectionable from the standpoint of appearance of the product. Neutral saline solutions prepared for intravenous injection have also developed these flakes and have even become toxic because of changes in alkalinity. Serums have undergone alkalinity shifts with accompanying changes in composition, color, and potency; and culture media have shown changes in pH sufficient to render them useless. Since the source of most of these objectionable features has been traced to the quality of glass from

which the containers were made, reliable methods for determining the chemical durability of glass are needed.

The selection of a method depends upon the circumstances involved. In the case of popular beverages the effect of flakes on their appearance is the important factor. For pharmaceutical preparations the absence of toxic effects is the prime consideration. Freedom from change of pH may be the vital factor in preserving culture media. In seeking suitable means for evaluating the relative suitability of glass containers for storing liquids, much attention has been given to determining the quantity of alkali extracted from the inner surfaces by distilled water. The question arises whether this determination offers a satisfactory criterion for durability comparison, but because of the extensive use which has been made of this method an investigation was undertaken of some of the factors affecting it.

At first glance this evaluation would seem to be a simple question of an alkali titration or of a conductivity measurement, with few precautions necessary for obtaining reproducible and comparable results. Such is far from being the case. Since there is no suitable method for measuring the area of the inner surface of the containers, it is obvious that bottles of equal capacity and similar shapes **are** the only ones that can be readily compared. Furthermore, it cannot be too strongly emphasized that this test is not one of true solubility [1].[1] The test involves a decomposition of the glass and a subsequent solution of some of the decomposition products, followed in some cases by mechanical removal of insoluble materials (flakes) from the attacked area. This type of reaction is highly susceptible to slight differences in experimental conditions, such as temperature [1, 2, 9] and pH [2]. However, assuming that these factors are adequately controlled, certain other precautions for titrating the alkali extracts are necessary. Since these precautions, in much of the work reported, have been overlooked or disregarded, the present work was undertaken in an attempt to clarify the situation and to show what is necessary to obtain comparable results.

II. TITRATIONS OF AQUEOUS EXTRACTS FROM GLASS BOTTLES

1. EXPERIMENTAL PROCEDURE

New commercial bottles were rinsed three times and filled to their rated capacity with distilled water, covered with Pyrex covers, heated at 100° C in a covered boiler for 24 hours, and cooled to room temperature. The alkali extracted from the inner surface was then determined by titration. The standard, approximately 0.02 *N*, sodium hydroxide and sulfuric acid solutions were prepared by the usual procedures for minimizing the quantity of carbon dioxide present. The sodium hydroxide was standardized potentiometrically against potassium acid phthalate (NBS Standard Sample No. 84) and the sulfuric acid standardized against this sodium hydroxide.

All the titration data obtained with organic indicators were compared with the values obtained potentiometrically, using the saturated

[1] Figures in brackets indicate the literature references at the end of this paper.

calomel half-cell and glass electrode as reference and indicator electrodes, respectively. The emf measurements were made with a Leeds and Northrup portable potentiometer electrometer. The glass electrode was prepared by blowing a small bulb of Corning 015 glass [3] on the end of a soft glass tube and filling the bulb with mercury [4] for the electric connection. Although metal-filled glass electrodes are not considered as reliable for precise work as the solution-filled types, they were satisfactory for the present investigation.

2. FILTERED SOLUTIONS

(a) EFFECT OF CARBON DIOXIDE

Since glass is a fused mixture of strong, basic oxides, such as Na_2O and CaO, and weak acidic oxides, such as SiO_2 and B_2O_3, any attack

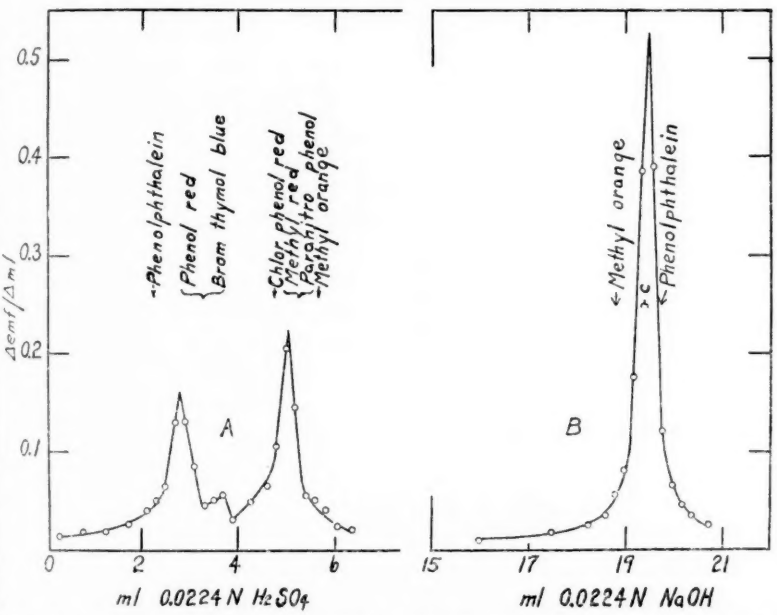

FIGURE 1.—*Comparison of potentiometric titrations with titrations made to the end point of seven organic indicators.*

A, Direct titrations. *B*, Back titrations after removal of CO_2 by the addition of 25.0 ml of 0.0224 *N* H_2SO_4, and exhaustion under reduced pressure. (Bracket indicated by *C* shows the titration spread for all the indicators from paranitrophenol to phenol red.)

on the glass by water will result in an alkaline solution. Such solutions when exposed to the atmosphere react readily with carbon dioxide, and, as a result, all unprotected bottle extracts absorb from small to appreciable amounts of carbon dioxide. The results of a direct titration made potentiometrically on a filtered bottle extract are shown in figure 1 (*A*) and table 1. The double end point is characteristic of solutions containing carbon dioxide.

TABLE 1.—*Typical potentiometric titrations (direct and back) of 100-ml filtered water extract from American Ceramic Society bottle glass No. 1, for comparison with titrations made on aliquots, using dye indicators.*

[25.0 ml of 0.0224 *N* H_2SO_4 was added to the extract prior to the back titration]

Direct titer			Back titer		
0.0224 *N* H_2SO_4	emf	Δemf/Δml	0.0224 *N* NaOH	emf	Δemf/Δml
ml	*Volts*		*ml*	*Volts*	
0.0	−0.045		0.0	−0.439	
		0.014			0.002
.5	−.052		5.0	−.430	
		.018			.001
1.0	−.061		10.0	−.418	
		.018			.004
1.5	−.070		15.0	−.397	
		.026			.008
2.0	−.083		17.0	−.380	
		.040			.017
2.2	−.091		18.0	−.363	
		.050			.024
2.4	−.101		18.5	−.351	
		.065			.035
2.6	−.114		18.7	−.344	
		.130			.055
2.8	−.140		18.9	−.333	
		.130			.080
3.0	−.166		19.1	−.317	
		.085			.175
3.2	−.183		19.3	−.282	
		.045			.385
3.4	−.192		19.5	−.205	
		.059			.390
3.6	−.202		19.7	−.127	
		.055			.120
3.8	−.213		19.9	−.103	
		.030			.065
4.0	−.219		20.1	−.090	
		.050			.045
4.5	−.244		20.3	−.081	
		.065			.035
4.7	−.257		20.5	−.074	
		.105			.026
4.9	−.278		21.0	−.061	
		.295			
5.1	−.319				
		.145			
5.3	−.348				
		.055			
5.5	−.359				
		.050			
5.7	−.369				
		.040			
5.9	−.377				
		.023			
6.2	−.384				
		.020			
6.5	−.390				

Upon removal of this carbon dioxide by the addition of 25.0 ml of the standard sulfuric acid (a quantity known to be in excess of the alkali in the extract), heating, boiling under reduced pressure, and then titrating the excess acid, a marked change appears in the characteristics of the potentiometric titration curve. The results are shown in figure 1 (*B*) and in table 1. A comparison of the curves in figure 1 for the direct and back titrations emphasizes certain facts. The direct titration, *A*, shows the glass extract to be partially buffered, with relatively small voltage changes accompanying each addition of the titrating solution near the end points, while the back titration, *B*, in which the extract is unbuffered, shows much larger voltage changes per unit of addition. From these facts it is evident that the choice of an indicator which will give the correct answer by the direct titration is more limited than for the back titration.

(b) CHOICE OF INDICATOR

The end points for seven indicators used in direct and back titrations on 100-ml aliquot portions of a composite bottle extract are given in table 2, which also gives the results of potentiometric titrations on the same solution. It is apparent from this table that among the seven indicators only three—namely paranitrophenol, methyl red, and methyl orange—give end points in direct titration which approach that obtained by potentiometric back titration. Methyl red, which has been used for this titration [5], goes through a series of color appearances and fade-outs, making it difficult to use. However, if one waits for the fade-outs and continues to titrate until a permanent red persists, consistent results can be obtained, although they are still below the value obtained by the back titration. For the back titration all the indicators, with the exception of phenolphthalein and methyl orange, give end points within 0.15 ml of the same value and which are very close to the end point obtained potentiometrically.[2]

TABLE 2.—*Titration values obtained with the organic indicators in "direct" and "back" titrations for comparison with the values obtained potentiometrically*

Indicator	pH range	0.0224 *N* acid		Color	
		Direct titer	Back[a] titer	Base	Acid
		ml	*ml*		
Phenolphthalein	8.3 to 10.0	2.30	5.30	Pink	Colorless.
Phenol red	6.8 to 8.2	3.30	5.50	Red	Straw yellow.
Bromthymol blue	6.0 to 7.6	3.30	5.55	Blue	Do.
Paranitrophenol	5.0 to 7.0	5.20	5.62	Yellow green	Colorless.
Chlorphenol red	4.8 to 6.4	4.85	5.63	Purple	Straw yellow.
Methyl red	4.4 to 6.0	5.2	5.60	Straw yellow	Red.
Methyl orange	2.9 to 4.0	5.7	6.2	Orange yellow	Do.
Potentiometric	----------	[b] 2.8 5.0	5.5	----------	

[a] Values in this column were obtained by subtracting from 25.0 the number of milliliters of 0.0224 *N* NaOH required for full color change for indicators for the back titration.
[b] Double end point (see fig. 1).

The value obtained potentiometrically for the direct titration is approximately 0.5 ml lower than the value obtained by back titration. This difference may be due to interference of carbon dioxide and insoluble materials in the alkaline solution.

3. EFFECT OF SUSPENDED MATTER

Many bottles yield considerable suspended material (flakes) when digested with distilled water. A sample of these flakes taken from bottles made of American Ceramic Society bottle glass No. 1 [5] had the following composition: [3]

	Percent
SiO_2	54.5
R_2O_3	8.9
CaO	8.4
MgO	28.3

In order to determine what effect they might have upon the direct and back titrations, flakes from 18 bottles which had been digested for 24 hours at 100° C were transferred onto a Jena glass filtering

[2] The reagents were standardized potentiometrically. If the standardizations had been made with each indicator independently, it is possible that the results might have agreed even more closely.
[3] Analysis was made by F. W. Glaze.

crucible, washed once, and then suspended in 500 ml of distilled water. Fifty-milliliter aliquot portions of this suspension were titrated potentiometrically. For the direct titration the value indicated was less than 0.10 ml of 0.0224 *N* acid; hence it can be reasonably concluded that the presence of these flakes will not cause any appreciable error or lack of reproducibility in the direct titration.

Two series of tests were made on the conditions affecting the back titration, one to ascertain whether or not the time of digestion was a factor and the other to determine what effect, if any, the quantity of excess acid added might have upon the results. Fifty-milliliter aliquot portions were digested in Pyrex beakers on the steam bath for 15 minutes, 30 minutes, and 3 hours with 25.0 ml of 0.0207 *N* H_2SO_4. The results obtained are plotted in figure 2 and show that alkali con-

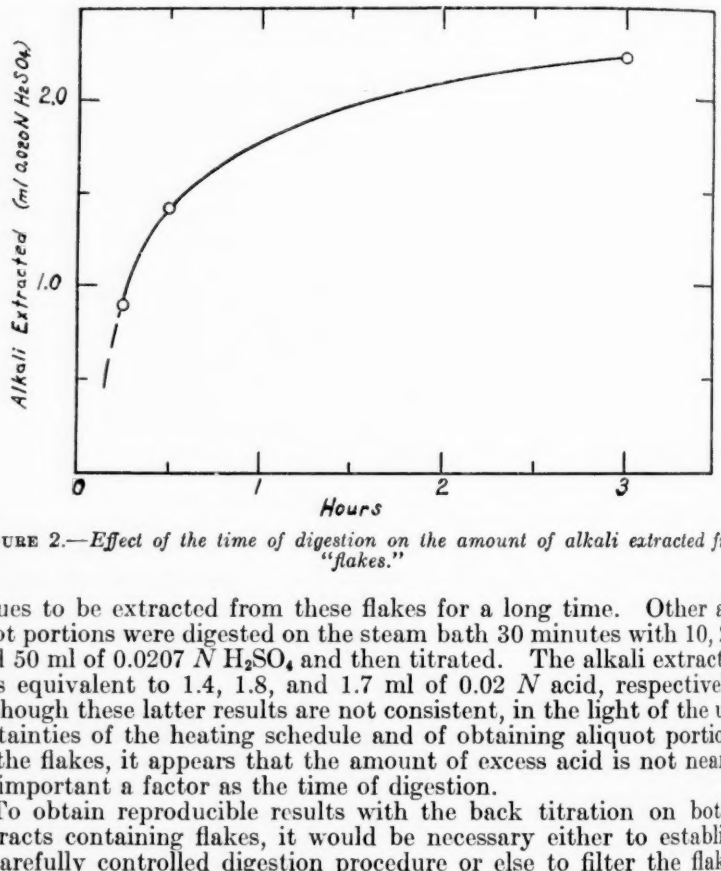

FIGURE 2.—*Effect of the time of digestion on the amount of alkali extracted from "flakes."*

tinues to be extracted from these flakes for a long time. Other aliquot portions were digested on the steam bath 30 minutes with 10, 25, and 50 ml of 0.0207 *N* H_2SO_4 and then titrated. The alkali extracted was equivalent to 1.4, 1.8, and 1.7 ml of 0.02 *N* acid, respectively. Although these latter results are not consistent, in the light of the uncertainties of the heating schedule and of obtaining aliquot portions of the flakes, it appears that the amount of excess acid is not nearly so important a factor as the time of digestion.

To obtain reproducible results with the back titration on bottle extracts containing flakes, it would be necessary either to establish a carefully controlled digestion procedure or else to filter the flakes before digestion with the excess acid. Since the former could not give a satisfactory answer, even though it were a reproducible one, and because of the indefinite amount of alkali extracted from the flakes, it is necessary to remove the flakes before digestion and evaluate them independently.

III. CONDUCTIVITY MEASUREMENTS OF AQUEOUS EXTRACTS FROM BOTTLES

1. INTRODUCTION

Having established some of the uncertainties in determining the alkalinity of bottle extracts by titration, the next step was to determine the merits of these alkalinity titrations as criteria of the relative durability of glass containers. Conductivity measurements of aqueous extracts have been suggested as a simple and accurate means of determining the chemical durability of glass containers, and this method was investigated [6, 7]. The conductance of the solution will vary approximately as its concentration. A deviation from a strictly linear relation will result from variations in the composition of the extract, since each kind of ion has its own specific conductance. As these water extracts are alkaline, they absorb CO_2 rapidly and must be protected.

2. EXPERIMENTAL PROCEDURE

The bottles were filled to their rated capacity with hot boiled distilled water and placed in the covered boiler at 100° C. At the end of a 24-hr. boiling period the bottles were removed one at a time from the boiler and tightly stoppered with cork stoppers, containing CO_2 guard tubes of Pyrex glass, so constructed that any moisture that might come in contact with the Ascarite in the tube could not drip back into the bottle. The specific conductivities of the extract were determined at 25° C. A pipette-type conductivity cell was used (fig. 3). The constant of this cell was 0.14173 mho (reciprocal ohm) cm. The resistance measurements were made using an a-c bridge similar to that described by Jones and Josephs [8]. All the conductivity determinations were corrected for the conductivity of the distilled water (1.043×10^{-6} mhos/cm).

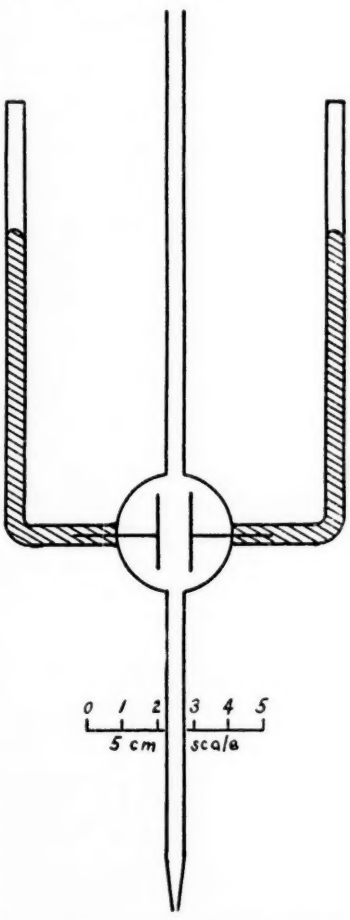

FIGURE 3.—*Pipette-type conductivity cell.*

Following the conductivity determinations, the extracts were titrated directly to the methyl red or the paranitrophenol end point. Then enough standard acid to make its total volume 25.0 ml was added, and the solutions were back-titrated potentiometrically.

3. DATA AND DISCUSSION

Typical results are given in table 3, in which column 3 gives the specific conductivities of the various extracts. The effect of absorbed CO_2 on the conductivity of the aqueous extracts cannot be emphasized too strongly. Even with protected extracts, the second determination has always been lower than the first by 1 to 2 percent of the originally determined conductivity. Since this difference was attributed to the absorption of CO_2, only the first determination is reported. Columns 4 and 5 give the alkalinities of the extracts as determined by direct and back titration, respectively. Since all the bottles except No. 6 were 4-fl-oz bottles (118-ml capacity), all the alkalinity results are reported as milliliters of 0.02 *N* acid required to titrate 118 ml of extract. Reporting the alkalinity in this unit is thought to give a clearer picture of the alkali extracted from a bottle than the usually accepted practice of reporting it as milligrams of NaOH per liter, inasmuch as the latter procedure involves multiplying all the titration errors by a factor of approximately 9 and also because alkalies other than NaOH are present and are titrated. All the titration results designated series *a* were obtained on the unfiltered extracts in the presence of flakes, if any had been formed, while those designated series *b* were obtained on extracts which had been filtered through a No. 40 Whatman filter paper after determining the conductivity of the extract. All the direct titrations were made with organic indicators and all the back titrations were made potentiometrically. The direct titrations of the unfiltered extracts, *a*, were made to the distinct permanent red of methyl red, and those on the filtered extracts, *b*, to the paranitrophenol end point.

TABLE 3.—*Conductivities and alkalinities of some aqueous bottle-extracts*

[Series *a*: unfiltered extracts, flakes are present, if any were formed; direct titration to methyl red end point. Series *b*: filtered extracts, flakes removed; direct titration to paranitrophenol end point. In all cases the back titrations were made potentiometrically]

Bottle number	Series	Specific conductance, *L*	0.02 *N* acid required per 118 ml extract		Δ *L*	Visible flakes	Type of glass
			Direct titer	Back titer			
1	2	3	4	5	6	7	8
		mhos×10^6	*ml*	*ml*	%		
1	*a*	95.6	5.37	6.27	7.7	Yes	Flint.
	b	88.2	4.97	5.23			
2	*a*	64.9	3.56	3.92	3.7	No	Blue.
	b	62.4	3.35	3.69			
3	*a*	102.7	5.09	4.94	3.3	do	Flint.
	b	106.2	5.18	5.04			
4	*a*	208.8	13.07	15.25	3.5	Yes	Do.
	b	201.6	12.44	12.83			
5	*a*	139.1	8.56	10.93	4.3	do	Do.
	b	133.1	7.99	8.61			
6	*a*	111.6	6.67	8.30	15.6	do	Do.
	b	94.2	5.55	6.41			
7	*a*	230.9	14.90	19.69	1.8	do	Do.
	b	226.8	14.54	14.72			
8	*a*	194.5	12.06	15.58	0.4	do	Do.
	b	193.8	12.42	12.85			
9	*a*	243.5	15.22	17.12	1.2	do	Green.
	b	246.4	15.44	15.77			
10	*a*	172.3	8.36	8.19	5.4	No	Amber.
	b	163.0	7.56	7.63			
11	*a*	284.3	18.43	20.19		Yes	Green.
12	*a*	164.4	9.18	8.95	4.5	No	Amber.
	b	172.1	9.14	9.47			
	a	92.2		5.09			
13	*a*	91.3		5.09	max	do	Flint.
	a	91.1		5.15	1.8		
	a	92.8	5.00	5.27			

It can be seen from figure 4 (data in columns 3 and 4 of table 3), that, with the exception of bottle extracts 3, 10, 12, and possibly 13, the conductivities are proportional to the alkalinities by direct titration. It should be noted that bottles 10 and 12 are amber bottles, and qualitative tests on their aqueous extracts showed the presence

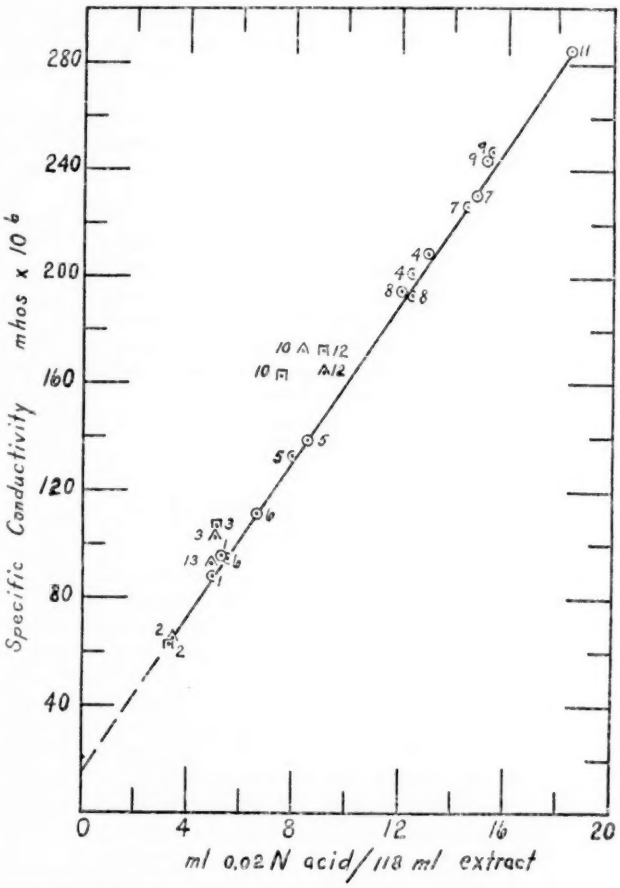

FIGURE 4.—*Conductivity versus alkalinity ("direct" titrations).*

1. Unfiltered extracts. Titrations to methyl red: ○, extract contained flakes; △, no visible flakes in extract.
2. Filtered extracts. Titrations to paranitrophenol: ☾, original solution contained flakes; ⌐, no visible flakes in original extract.

of sulfates, which would contribute to the conductivity but not to the alkalinity of the extracts. Both indicators appear to be equally good provided the titration to the methyl-red end point is continued to a permanent red. As this latter color is easily recognized, methyl red is to be preferred to paranitrophenol, since it is very hard to determine when the faint yellow color of the latter fades into a colorless solution.

Column 6 of table 3 shows the percentage differences in the specific

conductances of duplicate bottles (*a* and *b*). Although some large differences between duplicate bottles are indicated by both conductivity measurements and direct titrations, the conductivity always bears approximately the same ratio to the alkalinity. Therefore, these differences must represent real differences between the extracts and not errors in the determinations.

Such variations in the concentration of the extracts from duplicate bottles may occur as the result of slight variations in temperature during the extraction period, of differences in the interior surface of the respective bottles, or of a combination of both causes. As to the effect of variations in the temperature of the extracting medium, Bacon and Burch [9] have studied the effect of time and temperature when water, acid, and alkali are used as the extracting media. They concluded that there is no simple relation between temperature and the amount of alkali extracted by water. Later [10] they found that under certain conditions interpolations for differences in temperature can be made. After a critical study of their published data, it was concluded that the Arrhenius equation [11] for reaction rates is applicable to their results for aqueous extracts, provided the time is varied to produce equal attacks at each temperature. This relation has been found to apply to the attack of Na_2CO_3 solutions and water on a number of alkali borosilicate glasses [12, 13]. It has also been found to apply to the attack of 5-percent NaOH solutions on a wide variety of glasses [14]. This equation [11] is

$$\log k = -\frac{E}{2.303R}\frac{1}{T} + C = -\frac{b}{T} + C,$$

where k is the specific reaction rate, R is the gas constant, T is the absolute temperature, E and C are constants and b equals $E/2.303R$. The value of the quantity b, calculated from the data of Bacon and Burch, is 5,200 and if k at 100° C is taken as unity, then C becomes 13.937. Table 4 gives the calculated effect of certain temperature changes and shows that even small changes in temperature may introduce significant errors. Hence exact temperature control is needed, especially if one is to correlate short-time tests with actual service conditions. With the exception of three sets of duplicate bottles (Nos. 1, 6, and 10), the differences in conductivity shown in column 6 of table 3 could be accounted for by a temperature gradient of 0.5° C or less in our boiler.

TABLE 4.—*Calculated effect of temperature by Arrhenius equation on the rate of attack and the concentration of the resulting aqueous extract.*

[The rate of attack at 100° C is taken as unity]

Extraction temperature	Calculated "relative" rate of attack	Resultant decrease in concentration
° *C*		*Percent*
100.0	1.000	0.0
99.9	.992	.8
99.5	.958	4.2
99.4	.950	5.0
99.0	.917	8.3
98.0	.841	15.9
25.0	.0003	99.97

The series *b* results plotted in figure 5 (data in columns 3 and 5 of table 3) show that, with the exception of bottle extracts 3, 10, and 12, the conductivities of the various extracts are directly proportional to their respective alkalinities as determined by the back titration of the filtered extracts (flakes removed). Since all the conductivity determinations were corrected for the specific conductivity of the

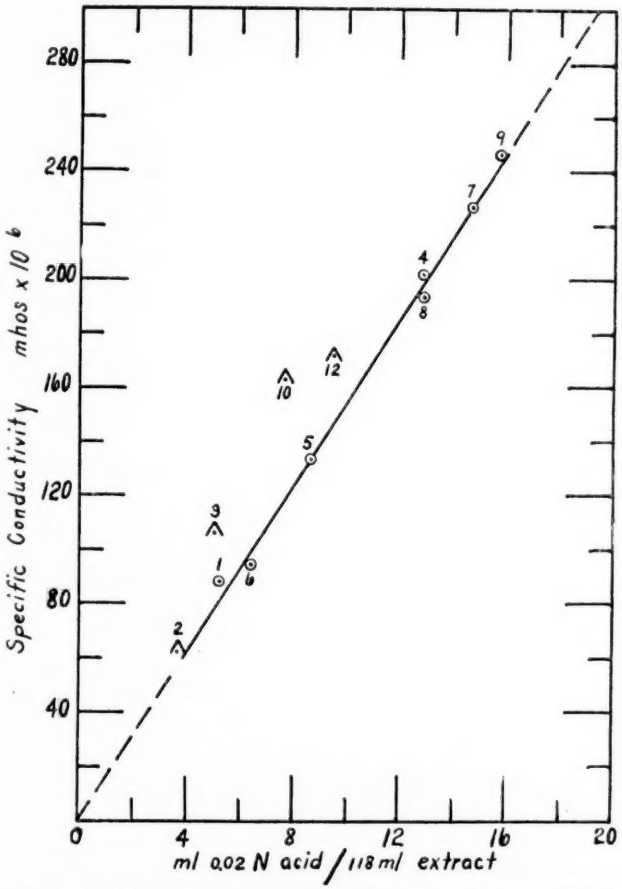

FIGURE 5.—*Conductivity versus alkalinity ("back" titrations on filtered extracts).* ○, original extract contained flakes; ∧, no visible flakes in original extract.

boiled distilled water, the line through the points in figures 4 and 5 should pass through zero if the specific conductivities of the extracts are directly proportional to their alkalinities. The fact that the line does pass through zero for back titrations (fig. 5) but not for direct (fig. 4) indicates that the difference between the direct and back titrations is real and that the back titrations are the more accurate.

The series *a* results in columns 3 and 5 of table 3 and in figure 6 show that no simple relation exists between the conductivities of the extracts and their respective back titrations in the presence of flakes.

As has been stated earlier in this paper, these titrations will include all of the bases originally in solution plus parts of the alkali initially in the flakes. The amount of the latter depends on the time of digestion on the steam bath, and the conductivity measures only the material originally in solution. It is evident from figures 4, 5, and 6

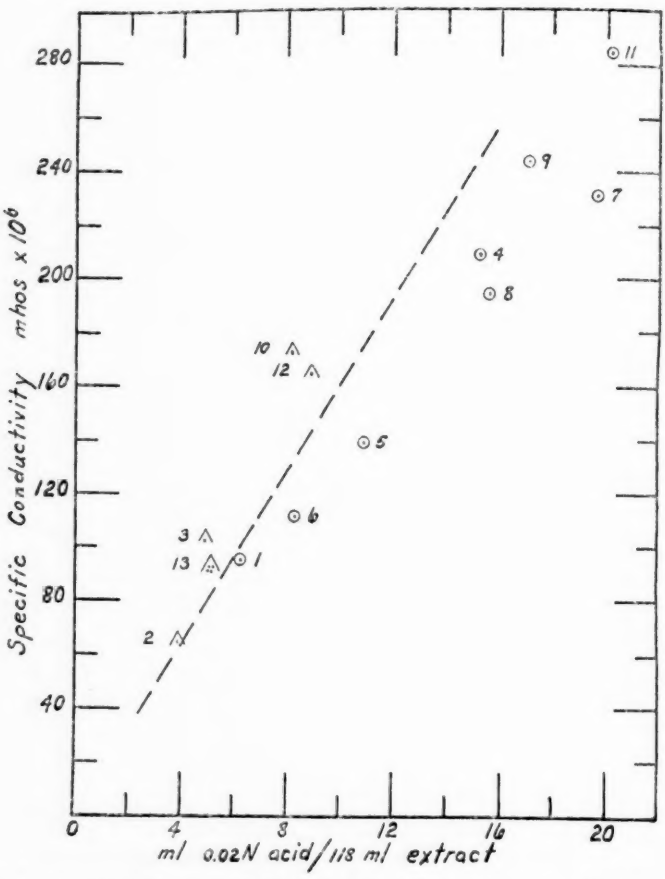

FIGURE 6.—*Conductivity versus alkalinity ("back" titrations on original unfiltered extracts).*

○, extract contained flakes; ∧, no visible flakes in extract.

that the amount of flakes produced by the attacking medium bears no simple relation to the alkalinity and conductivity of the resulting extract. Therefore, the flakes must be evaluated independently as a factor in the durability of glass containers.

From the foregoing considerations it is evident that, in any study of the chemical durability of glass containers, other factors besides the alkalinity and conductivity of the extracts must be considered. One such factor which logically presents itself is the determination of

the SiO_2 in the extracts.[4] Silica is the principal constituent of most glasses, and it has been demonstrated that with sodium silicate solutions of the same Na_2O concentration, the conductivity of the solutions increases as the SiO_2 concentration is decreased [15]. This fact may account for the position in figures 4, 5, and 6 of the points to the left of the line, which represent extracts from the five bottles which did not produce visible flakes in 24 hours at 100° C. The position of these points on the figure shows that the conductivity-alkalinity ratio, and hence probably the Na_2O:SiO_2 ratio, is higher in the extracts from the bottles which did not produce flakes than in the extracts from the other bottles. However, as has already been pointed out, in the case of extracts from bottles 10 and 12, the presence of sulfates may account at least in part for this effect. Of course, other factors, such as extremely low MgO, in the composition of these bottles might also affect the conductivity-alkalinity ratio of the extracts, since MgO is thought to be required for the formation of flakes.[5]

IV. SUMMARY

The amount of flakes produced in glass bottles as a result of attack by water bears no direct relation to the alkalinity or conductivity of the resulting extract. Therefore, the flakes must be evaluated independently as a factor in the durability of glass containers. For evaluating the liquid portion of the extracts, alkalinity or conductivity measurements may be used. If the alkalinity is measured, certain precautions must be observed in order to obtain reproducible results. For the direct titration of these aqueous extracts the choice of indicator is important because of the probability of contamination by CO_2. A more reliable procedure is to make a back titration after elimination of CO_2 by adding an excess of acid and heating and boiling under reduced pressure, in which case the choice of indicator is not so critical. In the latter case the flakes, which are often plentiful in aqueous bottle extracts, must be removed prior to heating in order to prevent their affecting the results.

Both the titration and conductivity methods are capable of giving reproducible results. Although they may not place a given series of bottles in exactly the same order of resistance to attack by distilled water, each gives data which will differentiate between bottles of equal capacities and shapes. Within reasonable limits it can be stated that the greater the titration value or the higher the conductivity of the aqueous extracts from the container, the less satisfactory is the durability of the glass. Since the titration procedure indicates only the alkali extracted from the glass, while the conductivity method is sensitive to all the ions dissolved, the conductivity method probably gives the fairer comparison between containers made from all types of glasses.

However, the question still remains whether the resistance offered by glass to the attack of water is a satisfactory criterion of durability. The enormous difference observed between the attack upon optical glasses by buffer solutions near neutrality and that produced by

[4] Quick, easy methods have been developed for the colormetric determination of SiO_2. While the application of such methods would require the use of a good spectrophotometer, they would have the advantage that SiO_2 could be conveniently determined in acidic, basic, and neutral extracting media over a wide range of pH [2, 14], provided interfering ions, such as phosphates, were absent. If additional data are required, Na_2O, CaO and MgO, and SO_3 could be determined.

[5] Private communication from W. R. Lester, Maryland Glass Corporation, Baltimore, Md.

water [14] indicates that data obtained for water must not be used too freely in predicting resistance to attack by aqueous solutions.

The authors are indebted to A. N. Finn for his helpful suggestions and cooperation during the progress of this investigation.

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EFFECT OF ROUGHNESS OF CAST-IRON BRAKE DRUMS IN WEAR TESTS OF BRAKE LININGS

By Rolla H. Taylor and William L. Holt

ABSTRACT

Five representative types of commercial brake linings were tested against centrifused cast-iron brake drums having widely different values of roughness. It was found that (1) the rate of wear of brake lining is an increasing function of the initial roughness of the drum, (2) the actual wear characteristics of a given lining are a function of the character of the surface of the drum and of the type and quality of the lining, (3) the roughness of the drums, in general, has a greater effect on the wear of woven linings than on the wear of molded linings, and (4) the rate of wear of brake linings tested against relatively smooth drums becomes practically constant after the first few hundred stops. For relative wear tests a drum of specified type and finish, having a roughness of not more than 15 microinches root mean square is recommended.

The effect of the roughness of brake drums in service is probably similar to that obtained on the testing machine but less in magnitude.

The coefficient of friction appears to be slightly lower the rougher the drum, but for all practical purposes the effect of roughness on the coefficient of friction may be neglected.

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I. INTRODUCTION

Experience in the testing of brake lining by means of the small inertia testing machine described elsewhere [1] [1] clearly indicates that control of the characteristics of the drum surface is necessary for reproductible determinations of wear. The rates of wear of some linings have been observed to vary by more than 300 percent when tests have been made with drums differing widely in roughness. Roughness, however, is by no means the only condition of the drum

[1] Figures in brackets indicate the literature references at the end of this paper.

surface which may affect the wear of brake linings, but it is probably the most important from the standpoint of relative wear if the drums used are all of the same type and kind.

Wear has always been one of the major problems of the brake-lining industry, and many of the factors related to it have been extensively studied. In fact, it would be presumptuous to assume that any one factor had not at least been considered by someone. Brake drums have been improved periodically, and with the development of more convenient methods for measuring surface roughness and of better grinding equipment the quality of the finish is being improved. The effect of the roughness of brake drums on the wear of the linings has been recognized for some time. It is only within the last few years, however, that convenient methods have been available for evaluating roughness of metal surfaces, and, so far as is known, no quantitative data have hitherto been published on the relation between the roughness of drums and the rate of wear of the linings. The present investigation was undertaken to study this relation.

Five representative linings were tested against a number of brake drums which covered a considerable range of roughnesses. Superfinished drums and the smoothest of the ground drums represented one extreme and turned drums the other, while drums of intermediate characteristics were prepared by grinding in different ways.

II. METHOD OF TEST

The tests were made by means of the small inertia-type machine mentioned above, which has been the subject of a previous publication. The linings were selected so as to be representative of those in commercial use. Drum surfaces were prepared so that their respective roughnesses differed over wide limits but other factors which might have affected the wear were kept as nearly constant as practicable.

1. EVALUATION OF DRUM SURFACES

The general problem of evaluating a metallic surface should take into account not only the roughness but also the microstructure of the material at the surface, the flaws which may be present—such as holes, inclusions, hard spots, peaks, and scratches—the method by which the surface was finished, and the waviness of the surface. Swigert [2], in "The Story of Superfinish", lists a number of terms used for describing the finish of surfaces and gives precise definitions of them, which have been formulated in connection with the work of the Chrysler Corporation.

Many of these characteristics were eliminated from consideration in the present investigation because the primary concern was relative wear and because centrifused cast-iron drums were used throughout. Under the circumstances the principal concern was with deviations of the surface of the drum. Shurig [3] suggests three factors—namely, roughness, waviness, and flaws—which should be considered in evaluating the deviations of a surface. For present purposes the method of finish was added to this list, since it affected the character of the roughness. Of these four factors roughness was the only one given a numerical evaluation. The method of finish was considered in the presentation of the results. Waviness and flaws, however,

were not found to be significant except possibly in one or two cases.

The evaluation of the roughness of surfaces has been greatly facilitated by the recent development of the Profilometer [4], the profilograph [2], and the Surface Analyzer [5]. An American Standard for Surface Roughness [6] has been proposed and is designed to enable the roughness of a surface to be readily measured and specified within close limits.

The roughness of the brake drums which were used in the present investigation was measured by means of a Profilometer. Observations were made on each drum before and after a test. The measurements after a test were not altogether satisfactory, however, because minute score marks were sometimes produced in the drums by the linings. The slight scoring which took place apparently had no effect on the rate of wear of the linings but, it did cause the Profilometer readings made after test to be unreliable from the standpoint of relative values.

The Profilometer consists primarily of a tracer element having a diamond point 0.0005 inch in radius and a small coil which vibrates in a magnetic field as the tracer point is drawn over a surface. The voltage generated by these vibrations is proportional to the roughness and is impressed on a meter which is calibrated to read the root mean square (rms) value of roughness in microinches.

It was not to be expected that the roughness of the surface of any one drum would be uniform, but rather that it would vary from spot to spot. Actually the needle of the Profilometer meter vibrated over a range as the tracer point moved over the surface. The observer estimated the average high and average low values. The sum of the average high and average low values divided by two was taken as the roughness. The deviation of the high and low averages from the evaluated roughness ranged from approximately 2 microinches rms for the smoothest drums to approximately 15 microinches rms for the roughest drums.

The rms value of roughness [6] is defined as the square root of the average value of the squares of the perpendicular distances of points on the surface from some mean reference plane. Swigert [2] gives the ratio of rms values to the maximum values as from 1/3 to 1/5.

The Profilometer does not measure surface deviations when the frequency of the recurrent or random irregularities is less than about 100 per inch. Consequently it does not evaluate flaws or waviness. The surface deviations resulting from waviness can be measured by means of a conventional dial gage of appropriate sensitivity. Such measurements, however, were not made in the present work.

2. PREPARATION OF BRAKE DRUMS

Thirty centrifused cast-iron drums were employed in this investigation. Twelve of these drums had been in use for about 3 years and had been refinished several times. Twelve were new commercially turned drums and six were new superfinished drums. Each of the new drums was used to make one test before it was ground.

Except for these initial tests, each drum was wet-ground on a Heald grinder, No. 4927, type 7, style F, before using it for a test. The speed of the grinding wheel was 6,000 rpm, and the speed of the work was 160 rpm in the opposite direction. The rate of the feed can be set at 26 and 72 inches per minute; both feeds were used in the

course of the work. The thickness of the cut was regulated by the operator of the grinder to get the desired result. In order to get the smoothest drums, it was necessary to let the machine run after the final cut had been taken until contact between the grinding wheel and the work had practically ceased. Three grades of 5-inch hard-bonded silicon-carbide grinding wheels were used at different times. They were Norton wheels Nos. 3740–J5, 3760–J6, and 3780–J6 and were of medium open structure with grit sizes 40, 60, and 80, respectively.

Considerable difficulty was experienced in preparing ground drum surfaces of the desired degrees of roughness, particularly surfaces with roughnesses below 20 microinches rms and above 50 microinches rms. The superfinished drums and the best of the ground drums had a roughness between 10 and 15 microinches rms, and the commercially turned drums had a roughness of approximately 100 microinches rms. The majority of the ground drums were given roughnesses ranging between these two values by using different combinations of wheels and speeds. It was found that the smoothest surface could be obtained by using the 3760–J6 wheel with a feed of 26 inches per minute and by letting the machine run until the last cut was completely ground out. It was found necessary to dress the wheel frequently.

The general procedure was to grind all of the available drums at one time, under given conditions, measure the surface roughness, and use them to make tests on one or all of the five linings. Each time a group of drums was reground the method of grinding was adjusted in accordance with the above variables to give the roughnesses desired for the next set of tests. The drums and linings were used in such combination that each lining was tested against a series of drums covering the desired range of roughness.

3. SELECTION OF BRAKE LININGS

The five brake linings used in these tests were selected as being representative of the higher grades of the different types of commercial linings in common usage at this time. A description of each lining is given in table 1.

TABLE 1.—*Description of brake linings*

Lining No.	Type	Color	Metal in lining	Structure	Grade[1]
48	Rigid molded	Tan	None	Granular	Good.
62	do	Black	Brass particles	Hard, dense	Excellent.
76	Flexible woven	Tan	None	Loosely woven	Good.
160	Flexible molded	Brown	do	Tough, resilient	Excellent.
161	Flexible woven	Tan	Zinc wire	Dense, closely woven	Do.

[1] This grading has no commercial significance but merely indicates the relative standing of these linings compared with a large number of linings tested by the National Bureau of Standards on a comparative basis.

4. TEST PROCEDURE

The wear of the brake linings was measured in terms of the reduction in thickness which was brought about by using specimens of the lining to stop the flywheel of the testing machine a given number of times. Test pieces of the lining having a 2- by 2-inch rubbing surface were clamped on the two shoes of each brake and were run against drums of measured roughness. Each test consisted of approximately

5,000 complete stops of the machine from 600 rpm at intervals of 1.5 minutes. The stopping of the machine under these circumstances was approximately equivalent to the stopping of an automobile, on the average, from a speed of 50 mph by means of the usual service brakes. The thickness of each piece of lining was measured at four designated points by means of a ratchet micrometer caliper. Measurements of thickness were made at the beginning of each test and at intervals of approximately 900 stops throughout the test. The lining and drum were cooled to room temperature before each set of measurements was made. Contrary to the procedure in testing under a specification [7], no wear-in period was employed before making the original thickness measurements because it was desired to obtain the initial as well as the sustained wear.

III. RESULTS AND DISCUSSION

The results of the measurements of wear are presented graphically. In figure 1 the wear is shown as a function of the number of stops and in figure 2 as a function of the roughness of the drums. Each curve in figure 1 represents the wear of a given brake lining against a given drum and the slope of the curve at any point represents the rate of wear of the lining at that point. The curves for the five linings are grouped in the five respective charts. The individual curves are designated by the initial roughness of the drums.

In figure 2 values for the wear are plotted against the initial roughness of the drums. Each solid circle in the figure represents the total wear of a given lining against a given drum at 3,000 stops and each corresponding open circle the sustained wear between the 1,000th and the 3,000th stop for the same test. The data from which figure 2 was plotted were taken for the most part from the curves of figure 1. As in figure 1, the curves of figure 2 are grouped in five charts for the five respective linings.

In plotting figure 1, curves for a few of the tests were omitted for the sake of clarity. Points from all of the tests, however, were plotted in figure 2.

1. RELATION OF WEAR TO NUMBER OF STOPS

As shown by the change of the slope of the curves in figure 1, there was a change in the rate of wear during each test. For tests made on the smoother drums the rate of wear decreased rapidly during the first few hundred stops to some value which remained practically constant for the remainder of the test. Tests on the rougher drums showed the same general characteristic, but the rate of wear continued to decrease throughout the entire test with the rate of decrease becoming less as additional stops were made. This is an indication that continued testing against any one drum would result in the rate of wear eventually reaching some value which is a constant for the lining. It should be noted, however, that in the case of rough drums several sets of lining might be worn out before this constant value is reached.

The high rate of wear at the beginning of a test was probably due in large part to the fine sharp edges of the finish marks on the newly finished drums and may be termed initial wear. These sharp edges, however, were soon worn off or dulled, and the rate of wear approached some constant value which may be termed the sustained wear.

Conner [8] notes the same phenomena in his studies of the relation of surface finish to the wear in internal combustion engines. Dayton [9] has defined the types of wear referred to in this paper as initial and sustained wear as cutting and abrasive wear, respectively.

The number of stops required for the rate of wear to become constant is dependent on the initial roughness of the drum and on the character of the lining being tested. For drums having a roughness

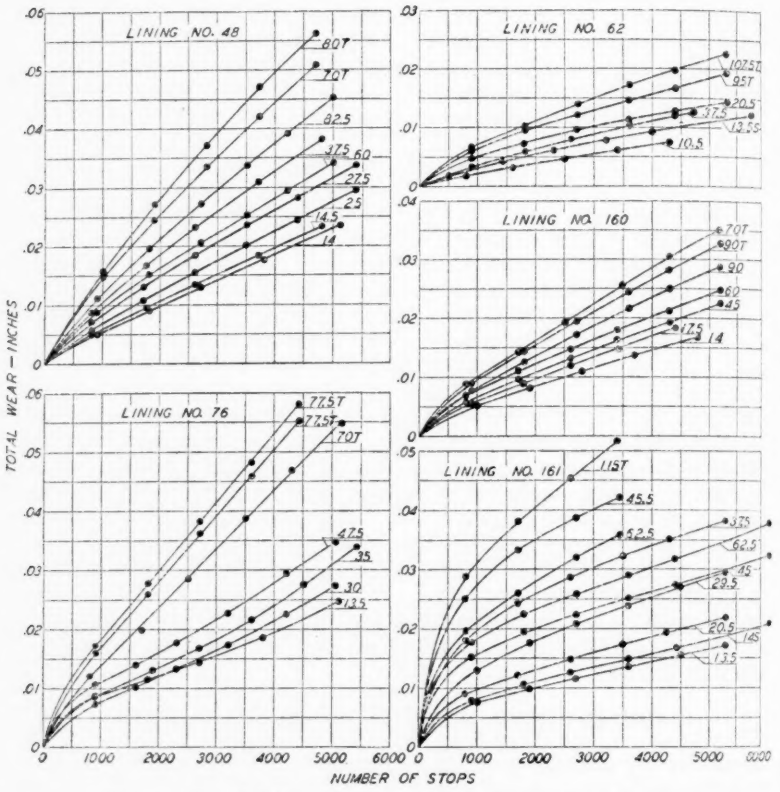

FIGURE 1.—*Relation between wear and the number of stops.*

Each individual curve is designated with a number representing the evaluated roughness of the drum on which the test was made. Curves marked *T* are for tests made on turned drums, those marked *S* are for tests made on superfinished drums, and the remainder are for tests made on ground drums.

of 60 microinches or more the rate of wear may become constant only after several thousand stops, while for relatively smooth drums having a roughness of 15 microinches or less the rate of wear may become practically constant in a few hundred stops. Hard dense linings, such as No. 62, apparently wear off and dull the rough edges of a drum much faster than softer linings, such as Nos. 48 and 76. Consequently, one may expect the rate of wear of the former to become constant much more rapidly than the latter, the initial conditions of the drums being the same.

Lining 76 differed in behavior from the other linings in that the rate of wear after the initial period (except for turned drums), showed

a slight increase throughout the period of test, as indicated by a slight upward trend of the curves in figure 1. This increase in the rate of wear was probably due to a progressive change in the lining on account of heat or other factors, whereby it became progressively more susceptible to wear. The fact that the curves for the three tests made on turned drums appear to be straight lines is probably due to the drums becoming smoother at a rate sufficient to offset the tendency

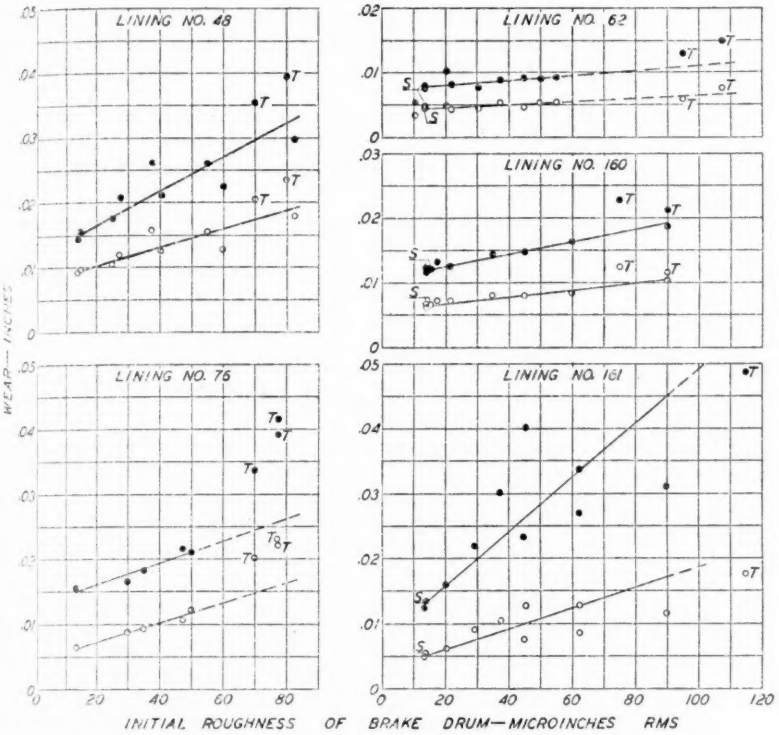

FIGURE 2.—*Relation between wear and the initial roughness of the drum.*

Solid circles represent the total wear at 3,000 stops. Open circles represent the wear between the 1,000th and 3,000th stop. Points marked *T* are from data for turned drums; those marked *S* from data for superfinished drums, and the remainder from data for ground drums.

of the wear to increase. This is borne out by the observation that the rate of wear for the tests of the other four linings, which were made on rough drums, decreased continuously throughout a test.

2. RELATION BETWEEN INITIAL ROUGHNESS OF DRUMS AND WEAR

Figure 1 gives a clear indication that the average rate of wear of linings increases with the initial roughness of the drums, since the majority of the curves fall in the order of increasing roughness. Figure 2, however, shows this relationship directly for the total wear and also for the sustained wear. As was mentioned previously, the total wear was taken as the wear which occurred during the first 3,000 stops. This number of stops was taken because it is approxi-

mately the number required in making the tests that have been established to determine the frictional characteristics of linings. A plot for 4,000 and for 5,000 stops similar to the plot for 3,000 stops in figure 2, as well as other methods of analyzing the data, apparently added nothing materially to the general picture.

The sustained wear was taken as the wear between the 1,000th and the 3,000th stop. This value is comparable with that which may be expected to occur on comparable drums during the determination of the frictional characteristics in accordance with a present specification [7]. For smooth drums the rate of wear becomes nearly enough constant after the initial wear-in period to give reproducible results.

The individual points plotted in figure 2 show considerable scattering, and the curves have been drawn as straight lines in the absence of any clear-cut indication of a more complex relation between the roughness and the wear.

The scattering of the data is to be expected since the drums differed not only in the amount of roughness, as indicated by the Profilometer, but also in the character of the surface irregularities which constituted the roughness. The turned drums, in general, caused greater wear in proportion to the roughness than did the ground and the superfinished drums. The determinations on turned drums are designated in figure 2 by points marked *T*. The majority of these points fall above the curves, which were drawn on the basis of the measurements on ground and superfinished drums.

The results of tests of linings 48 and 161 were less consistent than those of the other three linings. Two factors may have contributed to the wider spread of the data obtained for these linings—(1) they may have been more sensitive to differences in the character of the surface than the other linings, and (2) most of the rough drums used for testing these linings were ground at a different time from the drums used for the other three linings and with a more variable procedure and may, therefore, have differed from the latter by reason of some uncontrolled factor introduced by the grinding. Hershman [10], for example, reports that different degrees of surface hardness are obtained for intaglio printing plates as a result of different grinding procedures.

3. RELATION BETWEEN TYPES OF LININGS AND WEAR

A comparison of the curves in the five respective charts of figures 1 and 2 shows that the five types of brake linings tested have quite different wear characteristics. In general, lining 161 has a relatively high initial rate of wear and a relatively low sustained rate of wear while lining 48 has a relatively low initial rate of wear and a relatively high sustained rate of wear. The effect of roughness on the wear of the two woven linings, 76 and 161, is greater than it is on the three molded linings. The amount of wear for any one type of lining tested under given conditions is obviously dependent on the quality of the lining.

Considering only the tests made on smooth drums it appears that (1) the initial rate of wear is a function of the initial roughness and the type of lining, (2) for relative wear tests, the sustained rate of wear may be considered to be a function of the lining only, and (3) the total wear, which may be taken as an indication of the expected life of the

lining when run against a newly finished drum, is a function of the lining and of the initial roughness of the drum. For tests made on rough drums, the sustained wear continues to be a function of the initial roughness until the rate of wear becomes constant.

4. SELECTION OF DRUMS FOR COMPARATIVE WEAR TESTS OF LININGS

The foregoing results indicate that the roughness of drums used for comparative wear tests should be carefully controlled and that the method of finishing should be specified. From the general knowledge of the properties of surfaces, it may be taken for granted that the composition of the drums, the method of manufacture, and similar factors should also be controlled as closely as possible.

The use of a relatively smooth drum is advantageous for comparative wear tests, because fewer stops are required before the straight-line portion of the wear curve is reached. Furthermore, the smoother the drums the more consistent the results. Another advantage is that when linings are tested on smooth drums, the condition of the drum is probably more nearly comparable to that of the majority of similar drums in service. Even when drums are placed on vehicles in a relatively rough condition, they are usually well smoothed-up long before the lining is worn out and if not they will in most cases be smooth for the replacement linings. A maximum value of 15 microinches rms, for the roughness of brake drums for wear tests, has been included in a recent revision of the Federal Specification for Brake Linings.

5. EFFECT OF ROUGHNESS OF DRUMS ON WEAR OF BRAKE LININGS IN SERVICE

The results presented here are in agreement with the practical observation that the smoother the drum the longer the brake linings will wear. The initial period of rapid wear would probably be less in service than in these tests, because the ratio of lining area to drum area is about five times as great on actual brakes as on the test machine and the larger area of lining would smooth the drum faster. The results indicate, however, that where very rough drums are used a set of linings may be completely worn out, even in service, before the rate of wear becomes constant.

6. RELATION OF COEFFICIENT OF FRICTION TO ROUGHNESS OF DRUMS

Measurements of the coefficient of friction of the linings on the drums were made during the wear tests by the procedure indicated in the previously mentioned description of the machine. The results indicate that the rougher the drum the lower the coefficient of friction. The magnitude of the effect, however, is small compared with that of other factors which affect the coefficient of friction.

In order to establish any quantitative relation between roughness and coefficient of friction, it appears that (1) a great many more data would be required or (2) the test conditions would have to be controlled more closely.

IV. CONCLUSIONS

1. The rate of wear of brake lining is an increasing function of the roughness of the brake drum.

2. The relation between the roughness of drums and the wear of brake linings is a function of the type and quality of the linings. In general this function may be summarized as follows: (1) The ratio of wear to roughness seems to be greatest for woven linings and least for dense, resilient molded linings; (2) the initial rate of wear is greater for woven linings than for molded linings; (3) for tests made on smooth drums the sustained rate of wear is practically constant for a given type and quality of lining.

3. A drum of specified type and finish with a roughness of 15 microinches rms or less is recommended for relative wear tests. The advantages of such a drum are that (1) results can be more easily reproduced, (2) less time is required to make a test which will be truly indicative of the life of the lining, (3) the sustained wear ceases to be a function of the initial roughness or the number of stops and may be considered to be a function of the lining only.

4. The roughness of the drum has a slight effect on the coefficient of friction which for practical purposes may be neglected.

5. The effect of the roughness of brake drums on the wear of linings is probably less in service than on the test machine.

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WASHINGTON, August 1, 1941.

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LOCATING THE PRINCIPAL POINT OF PRECISION AIRPLANE MAPPING CAMERAS

By Francis E. Washer

ABSTRACT

The location of the principal point with respect to the intersection of lines joining opposite pairs of collimation index markers was determined for numerous precision airplane mapping cameras. Weak prism effect, present in most camera lenses, was measured with the Bureau's precision lens-testing camera and its influence on the location of the principal point considered. It was found that these cameras required adjustments ranging from 2 to 25 times the allowable tolerance of ± 0.03 mm in the location of the principal point.

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I. INTRODUCTION

Rapid advances in the use of aerial photography for map making have been accompanied by steady improvements in the airplane camera as a precision instrument. As a result of these improvements the increased accuracy obtainable on projects calling for planimetric mapping has made it feasible to use the same negatives for the preparation of topographic maps of the same area, thus eliminating the necessity of rephotographing the region.

The need for topographic maps is evidenced by the fact that the United States is the least thoroughly mapped of any of the great industrial nations.[1] Such maps are of prime importance in the laying out of new road systems and in the location of proper dam sites for drainage control or power developments. With these aims in mind, various governmental agencies have interested themselves in the problems of making the negatives obtained on one project more useful for further studies of the same region.

It was soon found that negatives from different sources did not usually lend themselves readily to stereo-photogrammetric plotting of topography. Some of these difficulties were quickly traced to large values of the distortion and low resolving power, but after these factors

[1] C. A. Hart, Air Photography Applied to Surveying, p. 2 (Longmans, Green & Co., New York, N. Y., 1940).

had been minimized by the establishment of minimum performance standards for the lenses used in aerial cameras,[2] some difficulties still remained that were traceable to the airplane mapping camera.

Chief among these difficulties were the inadequate and nonuniform methods of showing the location of the principal point of the camera on the negative. This point is the intersection of a perpendicular dropped from the rear nodal point of the lens with the focal plane, and the importance of its accurate location has been shown in a paper by I. C. Gardner.[3] To insure more reliable information on the location of the principal point on each negative, new rigid requirements [4] for airplane cameras were established giving detailed instructions regarding the manner of recording index marks on each negative at the moment of exposure. Such index marks are to have a definite relation to the principal point of the camera and also to appear at the same place on all negatives from every camera being used on governmental projects.

These index marks on the negative are made by devices called the collimation index markers, set in the center of each side of the rear opening of a precision camera. They are so arranged that when each successive exposure is made, the image of each marker will be registered and show on the negative as a fine radial line. The detail requirements are that, for a camera using 9- by 9-inch or 7- by 9-inch films or plates and having a lens of approximately 8 inches focal length, the lines joining opposite members of the two pairs of index markers shall intersect at an angle of 90 ° ± 1 minute [5] and shall indicate the location of the principal point with a probable error not exceeding ± 0.03 mm.

Since it has been a requirement for several years that all lenses and cameras used on many Government mapping projects be tested by the National Bureau of Standards, it was necessary that methods be devised for determining the location of the principal point of an airplane mapping camera. This has been done, and this paper presents a description of the method as well as a survey of the results of measurements made on a number of airplane mapping cameras.

II. METHOD

Analysis of the problems involved in the certification of a precision airplane camera indicated that modification of the existing precision lens-testing camera offered the best immediate solution. This apparatus has been previously described in a paper by Gardner and Case [6] and no detailed description will be given here, except to mention that it has been enlarged and now has 10, instead of 7, collimators spaced at 5 ° intervals. For the calibration of precision airplane cameras, only nine of these collimators are used. The optical bench that carries the apparatus for the testing of photographic objectives is lifted from its mounting, and a telescope is mounted on the rear portion of the frame thus vacated. This telescope is adjusted to parallelism with the central one of the nine collimators, and centered upon the cross that serves as the collimator target.

[2] Standard specifications (2d ed.) published by American Society of Photogrammetry on July 22, 1936.
[3] J. Research NBS **22**, 209 (1939) RP1177.
[4] United States Department of Agriculture Specification No. A-APC-1102 (as approved March 1940).
[5] This requirement specifying the angular positioning of the collimation index markers insures their registration in the same place on negatives from different cameras and makes possible the use of such negatives without the necessity of readjustment of the plotting machine.
[6] J. Research NBS **18**, 449 (1937) RP984.

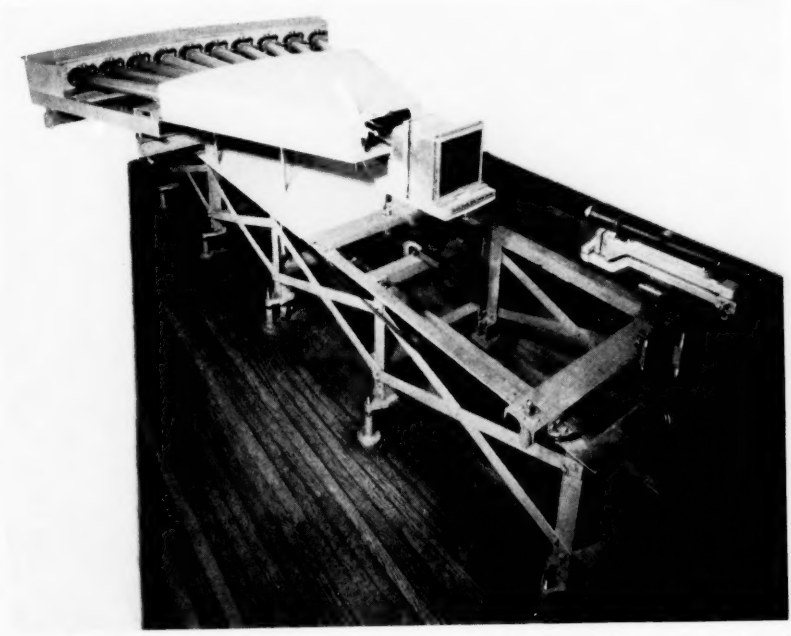

FIGURE 1.—*Precision lens-testing camera with an airplane mapping camera mounted in position for test.*

The airplane camera is rigidly mounted on the platform of a stand so located that the camera lens bears the same relation to the collimators that normally prevails for a lens when tested separately. The arrangement is shown in figure 1. The stand has adjustments that permit vertical and lateral translations and rotation of the platform carrying the camera about the vertical and the transverse horizontal axes. Adjustments are made until the camera is satisfactorily centered with respect to the collimator system and is pointed at the center collimator. A silvered flat glass plate is placed on the camera back so that it is pressed against the square flat metal plate surrounding the camera opening; the surface of this metal plate determines the focal plane of the camera. The telescope, the adjustment of which is left unchanged throughout the process, is now used as an autocollimator, and the focal plane of the camera is made perpendicular to the axis of the autocollimating telescope by small rotations of the camera platform. The rotation is so constrained that there is little likelihood of drift after the desired position is reached. Since the axis of the autocollimating telescope was initially set parallel to the axis of the center collimator, the focal plane of the camera is also perpendicular to the axis of the center collimator. Under these conditions, the cross that serves as a target for the center collimator will be imaged in the focal plane and indicate the point where parallel light directed perpendicular to the focal plane is imaged. This image, or the point determined by the image, will be referred to as the center cross. The targets of the remaining eight collimators are also imaged in the focal plane of the camera, and indicate the positions where parallel rays of light at 5°, 10°, 15°, and 20° on each side of the central ray are imaged.

When the camera has been properly alined, a photographic plate is substituted for the silvered glass plate in such a manner that its emulsion surface lies in the focal plane. On exposure, the images from the nine collimators are registered; simultaneously the collimation index markers are registered by means of four small flashlight bulbs arranged in front of the camera. To reduce error, four negatives are made, the camera being rotated 90° about its axis of symmetry between exposures.

III. INTERPRETATION OF NEGATIVES

1. PERPENDICULARITY OF COLLIMATION MARKERS

The first determination made from the negatives is that of the angle between the lines joining opposite collimation markers. For this purpose a piece of plate glass is used with four short radial diamond lines 90° apart cut in the surface near the end of a 4.5-inch radius. The error in the positioning of these marks does not exceed ±5 seconds. This plate is placed face down upon the emulsion side of the negatives in such manner that the radial diamond lines are nearly in coincidence with the index lines of the collimation markers. The plate and negative are then fastened firmly together and measurements made of the separation of each of the diamond lines from the corresponding index lines. Interpretation of the data thus gained yields the amount of departure from 90° of the angle between lines joining opposite collimation markers. If the departure does not exceed ±1 minute, the adjustment is adjudged satisfactory. It is noteworthy that over 90 percent of the precision cameras thus far measured have passed this requirement satisfactorily.

2. LOCATING CENTER OF COLLIMATION WITH RESPECT TO CENTER CROSS

The first step in the location of the principal point is the location of the position of the center cross with respect to the point of intersection of lines joining opposite collimation index marks. This point is called the center of collimation. Considering the lines joining opposite pairs of collimation index markers as the axes of a rectangular coordinate system with the center of collimation as origin, as is indicated in figure 2, the coordinates of the center cross are obtained from the negative. These measurements are made with a micrometer micro-

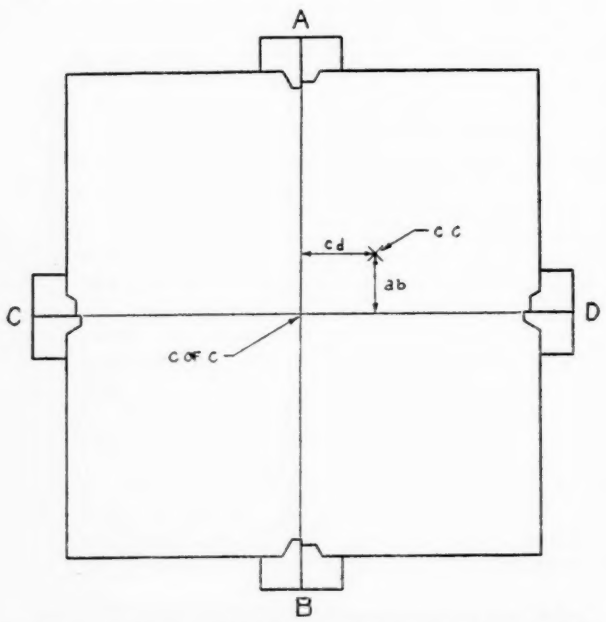

FIGURE 2.—*Schematic representation of a negative made with an airplane mapping camera.*

A, *B*, *C*, and *D* are the collimation index marks, *X* shows the position of the center cross (*CC*). The intersection of lines joining opposite pairs of collimation marks is called the center of collimation (*C of C*).

scope used, in conjunction with a slide of an optical bench, in a manner that permits measurement in a direction at right angles to the direction of movement of the slide carrying the negative. For convenience, the coordinate parallel to the line of flight is designated *ab*, and the one at right angles thereto *cd*. Measurements are made on each of the four negatives, and the final values of the coordinates are given by the average of the four determinations. Table 1 shows the magnitudes of these coordinates for a representative group of cameras and also the actual separation of the center of collimation and the center cross. The approximate probable error in the determination of each coordinate of the center cross with respect to the coordinate frame of the collimation index markers is ± 0.008 mm. The approximate probable

error in the determination of the distance between the center cross and the center of collimation is ±0.011 mm.

TABLE 1.—*Distance of center cross from center of collimation*

Camera number	*cd*	*ab*	$L=\sqrt{(cd)^2+(ab)^2}$
	mm	*mm*	*mm*
1	−0.08	+0.12	0.15
2	+.06	+.20	.20
3	+.10	+.08	.12
4	+.06	.00	.06
5	−.06	+.02	.06
6	−.04	−.06	.07
7	+.10	+.03	.10
8	−.75	−.19	.77
9	+.28	+.22	.36
10	+.07	+.07	.10

3. DISTANCE OF CENTER CROSS FROM PRINCIPAL POINT

The second step in the location of the principal point is to determine its position with respect to the center cross. For an ideal lens the principal point and the center cross coincide, since the principal point of a camera is defined as that point where a perpendicular dropped from the rear nodal point of the lens intersects the focal plane. In practice, the optic axis of a lens system is seldom an unbroken straight line. An axial ray may actually bend at each surface to form a broken line, and the ray that finally emerges may not be parallel to the incident ray. This effect is presumably produced by slight decentrations of the components of the lens system, and it can be approximated by treating the lens system as an ideal lens plus a weak prism.[7] Since this prism effect occurs in varying amounts in most real lenses, the center cross will be shifted slightly from the principal point when the negatives are made under the conditions described in section II.

Considering the camera lens as an ideal lens plus a weak prism, it is apparent that the images from all nine collimators are shifted from the positions they normally would have occupied in a direction determined by the orientation of the effective weak prism. The deviation of a given ray is a function of the prism angle and the angle of separation from the central ray. In figure 3, let C represent the center of an ideal lens, and CX_1 and CX_2 rays making equal angles, β, with the central ray, CO. Let O be the principal point of the camera and CO the principal distance, or focal length, f. If a weak prism of angle α be interposed between the lens and the focal plane, the points of intersection of rays CX_2, CO, and CX_1 are shifted to X_2', O', and X_1', the direction of shift being toward the base of the prism. The angle of the shift for each ray is given by ϵ_2, ϵ_0, and ϵ_1. From the diagram

$$O'X_2'=f[\tan\ (\beta+\epsilon_2)-\tan\ \epsilon_0]=f\lambda,$$

$$O'X_1'=f[\tan\ (\beta-\epsilon_1)+\tan\ \epsilon_0]=f\xi,$$

and

$$O'X_2'-O'X_1'=f(\lambda-\xi).$$

[7] A. H. Bennett, J. Opt. Soc. Am. and Rev. Sci. Instr. **14**, 235 (1927).

Table 2 shows the values of $f\ (\lambda-\xi)$ for a 210.00-mm lens with $\beta=20°$ for several values of the prism angle α. Values of ϵ_2, ϵ_0, ϵ_1, from which the values of $f\ (\lambda-\xi)$ are computed are also shown. The column $f \tan \epsilon_0$ shows the actual shift of O', the center cross from the principal point, O. In the table due allowance is made for the fact that the deviation of a ray passing obliquely through a thin prism is appreciably different from the deviation of a ray passing through a

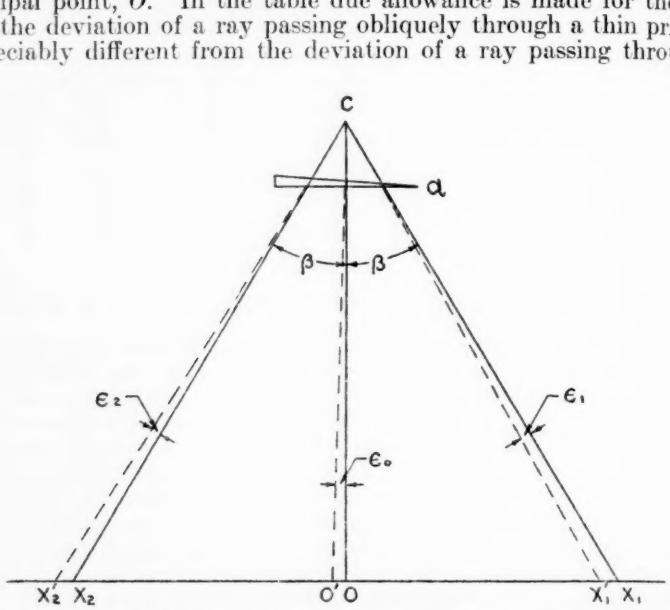

FIGURE 3.—*Effect of interposing a prism between lens and image plane.*

The solid lines show rays proceeding from C, the rear nodal point of the lens, to the image plane. The dashed lines show how these rays are deviated by a thin prism of angle α.

thin prism in the position of minimum deviation. This is evidenced by the differences in the values of ϵ_1, ϵ_2, and ϵ_0.

TABLE 2.—*Effects* [a] *of a weak prism combined with an ideal lens*

α	ϵ_1	ϵ_0	ϵ_2	$f\ (\lambda-\xi)$	$f \tan \epsilon_0$
Degrees	*Degrees*	*Degrees*	*Degrees*	*mm*	*mm*
0.01250	0.00693	0.00625	0.00693	0.0117	0.0229
.02500	.01385	.01250	.01385	.0233	.0458
.05000	.02771	.02500	.02772	.0468	.0916
.10000	.05538	.05000	.05546	.0935	.1833

[a] Computed values of the angular deviation of the axial ray and of rays making angle $\beta=20°$, with the axial ray for the combination of an ideal 210 mm lens and a weak prism of index 1.5 and angle α. The values of $f\ (\lambda-\xi)$ are given together with the computed value of the shift, $f \tan \epsilon_0$, of the center cross with respect to the principal point.

A similar table has been prepared for $\beta=15°$ and is used in conjunction with table 2 in determining the location of the center cross with respect to the principal point. In actual practice, the quantities $O'X_2'$ and $O'X_1'$ are measured from the negative and their difference forms a value of $f\ (\lambda-\xi)$ with which the shift of the center cross is obtained from the tables.

To avoid the tedious process of setting the collimators at precisely equal angles, it has proved more convenient in the evaluation of $f(\lambda-\xi)$ to combine the measurements from two negatives that were made with the airplane camera in positions 180° apart as measured around the axis of symmetry of the airplane camera. This procedure reduces the amount of computation and eliminates the necessity of compensating for the distortion of the lens, which is presumed to be symmetrical about the lens axis. The direction of shift of the center cross from the principal point is given by the algebraic sign of $f(\lambda-\xi)$.

The shift of the center cross on account of prism may be in any direction in the focal plane. Accordingly the coordinates *ab* and *cd* of the center cross with respect to the principal point are obtained by using two pairs of negatives, each pair of which gives one of the coordinates. The magnitudes of these coordinates, as well as the total shift of the principal point for a representative group of cameras, are shown in table 3. The approximate probable error in the determination of the distance between the principal point and the center cross does not exceed ±0.005 mm. As a matter of interest the approximate values of effective prism angle are also shown.

TABLE 3.—*Distance of center cross from principal point*

Camera number	*cd*	*ab*	$\sqrt{(cd)^2+(ab)^2}=f\tan\epsilon_0$	*f*	α
	mm	*mm*	*mm*	*mm*	*Minutes*
1	−0.02	+0.04	0.04	209.78	1.4
2	−.04	+.03	.05	209.67	1.6
3	−.05	−.03	.05	209.67	1.8
4	−.02	−.02	.03	210.22	1.0
5	+.06	+.07	.09	210.21	3.0
6	+.08	−.03	.09	209.50	2.9
7	+.01	.00	.01	209.65	0.4
8	−.04	+.01	.04	209.87	1.3
9	+.16	−.02	.17	210.93	5.4
10	+.03	+.01	.03	255.59	0.8

4. LOCATING PRINCIPAL POINT WITH RESPECT TO CENTER OF COLLIMATION

In section 3, the method of locating the center cross with respect to the center of collimation is given; in section 4, the method of locating the principal point with respect to the center cross is given. Combining the results of these two processes with due regard to the geometry of the configuration, we obtain the location of the principal point with respect to the center of collimation. Values of the separation distance for a representative group of cameras are shown in table 4. It is apparent that, for the majority of cameras as submitted for certification, the measured separation of principal point and center of collimation is considerably in excess of the tolerance of ±0.03 mm.

TABLE 4.—*Distance of principal point from center of collimation before adjustment of airplane camera*

Camera number	*cd*	*ab*	$\sqrt{(cd)^2+(ab)^2}$
	mm	*mm*	*mm*
1	−0.06	+0.08	0.10
2	+.10	+.17	.19
3	+.14	+.10	.18
4	+.08	+.02	.09
5	−.11	−.05	.12
6	−.12	−.02	.12
7	+.09	+.03	.09
8	−.71	−.20	.74
9	+.12	+.24	.27
10	+.04	+.06	.07

5. ADJUSTMENT OF AIRPLANE CAMERA

Each of the cameras submitted for examination and adjustment is provided with devices that permit transverse movement of the lens with respect to the metal plate carrying the index markers. On the basis of measurements of the type described, the principal point and the center of collimation are adjusted to coincidence by appropriate movement of the lens with respect to the metal plate bearing the index markers. After adjustment, the movable part is so doweled to the camera body that this adjustment will be preserved. On account of the difficult nature of this adjustment and the possibility of slight shifts during the doweling, the location of the principal point, with respect to the center of collimation, is also measured after the doweling, and if the separation does not exceed ±0.03 mm, the adjustment is considered satisfactory.

This method has been used on a total of more than 40 precision airplane mapping cameras that have been submitted for use on projects of the Department of Agriculture. In practically all instances, it was necessary to make adjustments, as the departure of the principal point from the center of collimation ranged in the various cameras from 2 to 25 times the allowable tolerance of ±0.03 mm, and the average separation was 0.30 mm, or 10 times the tolerance value.

WASHINGTON, August 23, 1941.

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MT6. Tables of Sine, Cosine, and Exponential Integrals, Volume II:
Values of these functions to 9, 10, or 11 significant figures from 0 to 10 at intervals of 0.001, with auxiliary tables.
(1940) XXXVII+225 pages; bound in buckram, $2.00.

MT7. Table of Natural Logarithms, Volume I:
Logarithms of the integers from 1 to 50,000 to 16 places.
(1941) XVIII+501 pages; bound in buckram, $2.00.

Payment is required in advance. Make remittance payable to the "National Bureau of Standards", and send with order, using the blank form on the page facing this one for the purpose.

Above prices are for delivery in the United States and its possessions and in countries extending the franking privilege. To other countries the price of MT1 is 65 cents and that of MT2, MT3, MT4, MT5, MT6, and MT7 is $2.50 each; remittance to be made payable in United States currency.

Copies of these publications have been sent to various Government depositories throughout the country, such as public libraries in large cities, and colleges and universities, where they may be consulted.

A mailing list is maintained for those who desire to receive announcements regarding new tables as they become available. A list of the tables it is planned to publish will be sent on request.